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Analysing the large amplitude oscillatory shear of the CROSS and CROSS–MAXWELL models with the aid of FOURIER transform rheology using the example of a solvent-borne alkyd primer

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ABSTRACT

This paper contributes to the theory behind the analysis of strain-controlled large amplitude oscillatory shear (LAOStrain) using FOURIER transform rheology as well as LISSAJOUS plots and PIPKIN diagrams. It applies LAOStrain to both a reduced form of the CROSS model (known as the “rCROSS model”) and a MAXWELL model whose viscous part is defined by the rCROSS model (reffered to as the “rCROSS-MAXWELL model” in this paper). The analytical determination of the loss modulus and higher harmonics of the rCROSS model as mathematical functions simplifies the discussion thereof. This in turn facilitates the determination of characteristic points which are directly related to material parameters and therefore enable the identification of both the material parameters of the rCross model and their physical significance. A method for identifying material parameters can be presented which do not require minimising residuals of a non-linear optimisation scheme. It was not possible to identify an analytical solution to the non-linear viscoelastic constitutive equations of the rCROSS-MAXWELL model, which are therefore solved numerically. The characteristic points identified for the rCROSS-MAXWELL model are based on the analytical solutions arrived at for the rCROSS and MAXWELL models. This means that it is also possible to both identify the material parameters of the rCROSS-MAXWELL model and determine their physical significance. The method of material parameter identification developed is explained using the example of a solvent-borne alkyd primer and the characteristic points determined for strain amplitude dependent storage and loss moduli.

1. Introduction

Sinusoidal loading is a common method of investigating material behaviour. In some cases, loads which result in strain, strain rate and stress are so small that material behaviour can be characterised using a linear operator. This regime is referred to as *small amplitude oscillatory shear* (SAOS) ([1–4]). In the case of higher loads it is no longer possible to express material behaviour using a linear operator. This regime is known as *large amplitude oscillatory shear* ([1–3,5–7]). It is also necessary to differentiate between strain- and stress-controlled large amplitude oscillatory shear (LAOStrain and LAOStress ([6,8–10])). In this paper LAOS is used as an abbreviation for LAOStrain. Stress is measured as a response to an imposed sinusoidal strain and decomposed into storage modulus G', loss modulus G'' and higher harmonics a_k and b_k using FOURIER *transform (FT) rheology* ([1,5,11–19]). These material functions can be used as a basis for conclusions concerning material behaviour as well as assumptions which provide a foundation for a material model. This paper presents an exemplary model of the LAOS behaviour of a solvent-borne alkyd primer [20] by applying a reduced CROSS model (known as the “rCROSS model”) and a MAXWELL model whose viscous part is defined by the rCROSS model (referred to as the “rCROSS-MAXWELL model” in this paper). The CROSS model was originally proposed by WAZER et al. [21] and CROSS [22] and it can generally be used to describe *shear-thinning* or *shear-thickening* phenomena. This paper only discusses shear-thinning behaviour, with the accompanying non-linear strain rate dependent properties necessitating the application of LAOS. Shear-thinning non-linear viscoelastic behaviour can be predicted too e.g. by the GIESEKUS model ([23–25]) and PHAN-THIEN–TANNER type models ([23,26,27]). Given the restriction of these physical non-linearities to remain within the geometrically linear regime, the work presented in this paper takes the time derivative to be the partial derivative and assumes total shear strain γ to decompose additively. This paper aims to evaluate one shear component τ of the stress tensor. Normal stress effects are not addressed. The structure of the paper is as follows: Section 2 presents measurement data for the LAOS behaviour of the solvent-borne alkyd primer. A brief introduction to the theory of small and large amplitude

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oscillatory shear is provided in Sections 3.1 and 3.2. Constitutive equations for the rCross model are summarised in Section 4 and used as a basis for the definition of characteristic strain rates. Section 5 presents the analytical calculation of loss modulus, higher harmonics and Lissajous plots. As a result of the analytical nature of those calculations material functions are expressed in terms of mathematical functions. This represents one of this paper's key benefits and is highly useful during many steps in phenomenological material modelling process as emphasised by Giacomin et al. [28]. Material functions also simplify the identification of material parameters [25]. In particular, analytically defined material functions enable the identification of so-called *characteristic points* (distinct points in material functions which are directly influenced by the parameters of the material model). This in turn facilitates the identification of material parameters based on their physical significance. The non-linear viscoelastic constitutive equations of the rCross-Maxwell model are presented in Section 6. Section 7 sees characteristic points identified for the Maxwell and rCross model used to determine characteristic points in the material functions defined for the rCross-Maxwell model. The LAOS behaviour of the solvent-borne alkyd primer is modelled in Section 8. The authors of this paper are therefore able to successfully demonstrate the deterministic identification of the material parameters of the rCross-Maxwell model with the aid of characteristic points.

2. LAOS behaviour of a solvent-borne alkyd primer

This paper is based on the example of the LAOS behaviour of solvent-borne alkyd primer "SP4" Bhavsar et al. [20], which is discussed and modelled in Section 8. The detailed description of both the primer material and method of preparation provided by Bhavsar et al. means that only the key facts need be mentioned here. Bhavsar et al. [20] used "medium oil alkyd (MOA) based on Soya DCO (dehydrated castor oil) fatty acid, 50% oil length resins MOA1 and MOA2 [...] to prepare the primer. The ingredients used in the primer formulation were soya lecithin, bentone SD1, red oxide pigment, extenders viz. steatite and dolomite and driers viz. cobalt octoate and zirconium octoate were of commercial grade. [...] Oleate salt of tallow triethylamine" was used as a wetting agent. The primer was processed using a steel ball mill. The pigment volume concentration stood at approx. 68.9% (57 weight%). Measurements of storage and loss moduli G'_{meas} and G''_{meas} are presented in Fig. 1.

Fig. 1 (a) shows that storage and loss moduli decrease as strain amplitude increases. This supports the application of a shear-thinning viscoelastic material model, for example a Maxwell model whose viscous part is defined by a reduced form of the Cross model.

3. Steady state stress response to strain-controlled sinusoidal loading

This section examines strain-controlled sinusoidal loading

$$\gamma(t) = \hat{\gamma}\,\sin(\omega t) \quad \text{with}:\ \hat{\gamma} > 0, \quad \omega > 0 \tag{1}$$

$$\dot{\gamma}(t) = \hat{\gamma}\omega\,\cos(\omega t) \tag{2}$$

and its general stress response $\tau(t)$ without reference to specific material models. In the following, it is assumed that transient stress reaches steady state

$$\tau_\infty(t) := \text{STEADYSTATE}\{\tau(t)|_{\gamma=\hat{\gamma}\,\sin(\omega t)}\} = \tau(t > t_0). \tag{3}$$

The STEADYSTATE{ } operator yields t_0. The latter defines the time during which the transient stress response is in steady state, and is a periodic function with strain load period $T = 2\pi/\omega$ which satisfies $\tau_\infty(t) = \tau_\infty(t+T)$. Sinusoidal loading can be differentiated into small and large amplitude oscillatory shear depending on load parameters ω and $\hat{\gamma}$.

3.1. Small amplitude oscillatory shear (SAOS)

Steady state stress in case of SAOS is given as

$$\tau_\infty(t) = \hat{\gamma}[G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)]. \tag{4}$$

Eq. (4) can be also transformed into ([29,30])

$$\tau_\infty(t) = G'(\omega)\gamma(t) + \frac{G''(\omega)}{\omega}\dot{\gamma}(t) = G'(\omega)\gamma(t) + \eta'(\omega)\dot{\gamma}(t) \tag{5}$$

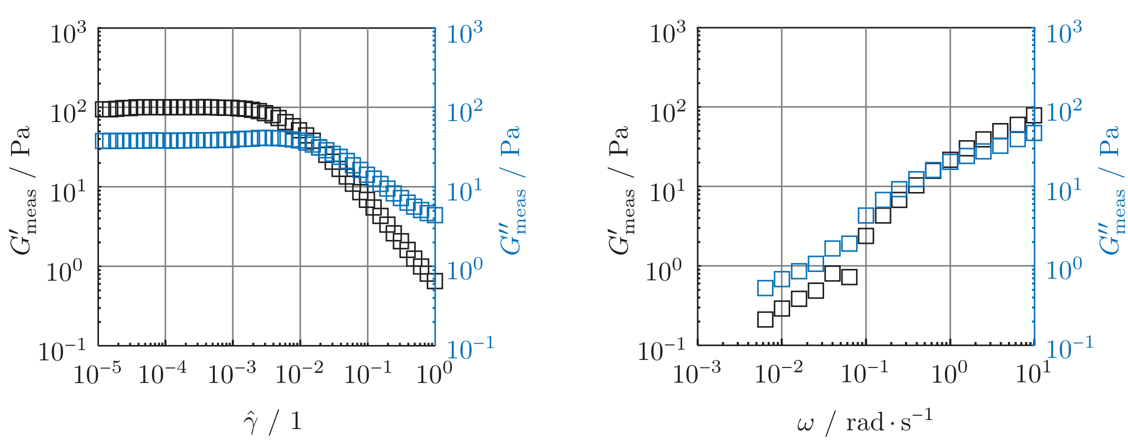
with reference to ([3,9,31–35])

$$\eta'(\omega) := \frac{G''(\omega)}{\omega}. \tag{6}$$

This defines the dynamic viscosity η' and directly motivates the representation of the steady state stress in terms of *dissipative scaling* ([3,6,7,9,28,34,36])

$$\tau_\infty(t) := \hat{\gamma}\omega[\eta''(\omega)\sin(\omega t) + \eta'(\omega)\cos(\omega t)]. \tag{7}$$

Sets $\{G', G''\}$ and $\{\eta', \eta''\}$ are both empirically defined material functions ([30,37]) which must not be functions of the strain amplitude in order to fulfil the conditions of linearity ([1,3,19]).



(a) Storage and loss modulus depending on the strain amplitude for $\omega = 10\,\frac{\text{rad}}{\text{s}}$

(b) Storage and loss modulus depending on the angular frequency in the linear viscoelastic range

Fig. 1. Measurements of the solvent-borne alkyd primer "SP4" from Bhavsar et al. [20].