On a constitutive model satisfying the Cox-Merz rule

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Abstract.

The dynamic behaviour of a non-linear visco-elastic polymer melt will be completely linear for small strain amplitudes and can be described with a (generalised) Maxwell model, this contrary to non-linear steady-state shear effects which can generally not be predicted with any linear model at all. For mono-disperse linear polymer melts it has been experimentally observed that the non-linear steady-state shear viscosity is equal to the dynamic viscosity at a shear rate identical to the oscillation frequency. As a linear Maxwell element can never satisfy this Cox-Merz rule, a modified Maxwell element is introduced consisting of a linear spring and a particular non-linear dashpot acting in series. The shear rate dependence of this G-dashpot corresponds with the frequency dependence of a linear Maxwell element. By relating the modulus of the Hookean spring to the non-linearity of the G-dashpot a new element called 'G-element' is created which satisfies the Cox-Merz rule over the complete frequency range. The generalised form of the G-model consisting of a number of G-elements parallel deviates at most 25% from the empirical Cox-Merz rule. For a characterisation of a polymer melt satisfying the Cox-Merz rule the parameters of this non-linear constitutive model can be found by fitting the linear dynamic behaviour with a number of Maxwell elements. This is illustrated for a LDPE melt ('Melt I') with an 8 modes G-model giving good results with regard to The Cox-Merz rule. Further stress growth and stress relaxation of 'Melt I' are computed with the model and are compared with experimental data. The stress growth prediction is fairly good apart from the overshoot while, although being factorisable, the prediction of the stress relaxation behaviour is moderate as the shear dependence does not correspond with what is experimentally observed.
**Notation.**

\[
\begin{align*}
G_0 & \quad \text{constant modulus} & \text{[Pa]} \\
G' & \quad \text{storage modulus} & \text{[Pa]} \\
G'' & \quad \text{loss modulus} & \text{[Pa]} \\
G^* & \quad \text{complex modulus} & \text{[Pa]} \\
G_d & \quad \text{dynamic modulus} & \text{[Pa]} \\
t & \quad \text{time} & \text{[s]} \\
\gamma & \quad \text{shear} & \text{[-]} \\
\gamma_0 & \quad \text{shear amplitude} & \text{[-]} \\
\gamma_0 & \quad \text{constant shear} & \text{[-]} \\
\gamma_s & \quad \text{shear of the spring} & \text{[-]} \\
\gamma_d & \quad \text{shear of the dashpot} & \text{[-]} \\
\dot{\gamma}_G & \quad \text{parameter in G-dashpot} & \text{[1/s]} \\
\delta & \quad \text{faseshift} & \text{[rad]} \\
\eta & \quad \text{viscosity} & \text{[Pas]} \\
\eta_0 & \quad \text{constant viscosity} & \text{[Pas]} \\
\eta' & \quad \text{storage viscosity} & \text{[Pas]} \\
\eta'' & \quad \text{loss viscosity} & \text{[Pas]} \\
\eta^* & \quad \text{complex viscosity} & \text{[Pas]} \\
\eta_d & \quad \text{dynamic viscosity} & \text{[Pas]} \\
\eta_s & \quad \text{steady-state viscosity} & \text{[Pas]} \\
\lambda & \quad \text{relaxation time} & \text{[s]} \\
\tau & \quad \text{stress} & \text{[Pa]} \\
\tau_0 & \quad \text{initial stress} & \text{[Pa]} \\
\omega & \quad \text{frequency} & \text{[rad/s]} \\
\cdot & \quad \text{material time derivative} \\
i & \quad \text{index for the i th element}
\end{align*}
\]
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Chapter 1: Introduction

Nowadays polymer materials play a very important role in many industrial fields. This is mainly caused by the relative easy processing of polymers, and therefore complex shaped products can be manufactured in mass production. To model the polymer processes like extrusion, injection moulding, film blowing and fibre spinning an accurate 3-D constitutive equation relating stresses to deformations is necessary. For that purpose a lot of integral and differential constitutive equations have been proposed to describe the behaviour of various thermoplastics (e.g. Lodge, Wagner), but an overall model based on molecular properties only has not yet been found.

For mono-disperse linear polymers there are some experimentally observed properties like the Cox-Merz rules, factorisibility and some other empirical relations. The aim of this study is to deduce a 1-D constitutive equation for shear flow starting from the empirical Cox-Merz rule [1] given by:

$$\eta_d(\omega) = \eta_s(\dot{\gamma} = \omega)$$ (1.1)

This means that the demanded constitutive equation has to have a non-linear steady-state behaviour corresponding with the linear dynamic behaviour. By adjustment of a linear constitutive model it is tried to gain an insight into polymers satisfying the Cox-Merz rule.
Chapter 2: Linear visco-elastic behaviour modelled with a Maxwell model.

2.1 Introduction.

Various types of visco-elastic behaviour of polymer melts can be described with a linear visco-elastic model like the (generalised) Maxwell model. This chapter gives a summary of the most essential properties of the single and the generalised Maxwell model.

2.2 The Maxwell model.

The single Maxwell element consists of a Hookean spring with modulus $G_0$ and a Newtonian dashpot with viscosity $\eta_0$ acting in series (see fig. 2.1).

Fig. 2.1: Maxwell model.

The relaxation time $\lambda$ of the Maxwell element is defined by

$$\lambda = \frac{\eta_0}{G_0} \quad (2.1)$$

while the constitutive equation can be expressed as

$$\dot{\gamma} = \dot{\gamma}_s + \dot{\gamma}_d = \frac{\dot{\gamma}}{G_0} + \frac{\tau}{\eta_0} \quad (2.2)$$
2.2.1 Stress relaxation.

At time \( t=0 \) the Maxwell model is subjected to a constant shear \( \gamma_0 \). Evaluating differential equation (2.2) with shear rate \( \dot{\gamma}=0 \) and with initial value \( \tau(t=0)=\tau_0=G_0\gamma_0 \) results in a relaxation stress

\[
\tau(t) = \tau_0 e^{-\frac{t}{\lambda}}
\]  

(2.3)

and a relaxation modulus

\[
G(t) = \frac{\tau(t)}{\gamma_0} = G_0 e^{-\frac{t}{\lambda}}
\]  

(2.4)

In fig. 2.2 the relaxation modulus is plotted double logarithmically versus the time. The relaxation modulus is independent of the shear \( \gamma_0 \).

2.2.2 Dynamic behaviour.

If a linear visco-elastic material is subjected to a sinusoidal varying deformation the stress will also vary sinusoidally with the same frequency but will be in front with \( \delta \) radians. In the case of shear the input deformation and the output stress can be expressed by:

\[
\gamma = \gamma_0 e^{i\omega t}
\]  

(2.5)

\[
\tau = \tau_0 e^{i(\omega t+\delta)}
\]  

(2.6)

The complex modulus and the complex dynamic viscosity are defined by:

\[
G^* = \frac{\tau}{\gamma} = G' e^{i\delta(\omega)} = G'(\omega) + iG''(\omega)
\]  

(2.7)

\[
\eta^* = \frac{\tau}{\dot{\gamma}} = \eta_d e^{i\delta(\omega)} = \eta'(\omega) + i\eta''(\omega)
\]  

(2.8)
If the linear visco-elastic behaviour is modelled with a single Maxwell element the storage and loss modulus, the storage and loss viscosity and the phase shift can be expressed as [2]:

\[
G'(\omega) = \frac{G_0 \omega^2 \lambda^2}{1 + \omega^2 \lambda^2} \tag{2.9}
\]

\[
G''(\omega) = \frac{G_0 \omega \lambda}{1 + \omega^2 \lambda^2} \tag{2.10}
\]

\[
\eta'(\omega) = \frac{G_0 \lambda}{1 + \omega^2 \lambda^2} \tag{2.11}
\]

\[
\eta''(\omega) = \frac{G_0 \omega \lambda^2}{1 + \omega^2 \lambda^2} \tag{2.12}
\]

\[
\tan \delta = \frac{G''}{G'} = \frac{1}{\omega \lambda} \tag{2.13}
\]

The dynamic modulus and viscosity are:

\[
G_d(\omega) = \sqrt{G'(\omega)^2 + G''(\omega)^2} = \frac{G_0 \omega \lambda}{\sqrt{1 + \omega^2 \lambda^2}} \tag{2.14}
\]

\[
\eta_d(\omega) = \sqrt{\eta'(\omega)^2 + \eta''(\omega)^2} = \frac{\eta_0}{\sqrt{1 + \omega^2 \lambda^2}} \tag{2.15}
\]

In fig. 2.3 the dynamic viscosity \(\eta_d\) is plotted double logarithmically against the angular frequency \(\omega\), which clearly visualises that the Maxwell element behaves Newtonian (viscous) in the low frequency range and Hookean (elastic) in the high frequency range:

\[
\omega \rightarrow 0 : \ \eta_d(\omega) \rightarrow \eta_0 \tag{2.16a}
\]

\[
\omega \rightarrow \infty : \ \eta_d(\omega) \rightarrow \frac{G_0}{\omega} \tag{2.16b}
\]
2.2.3 Stress growth.

At time $t=0$ the Maxwell model is subjected to a constant shear rate $\dot{\gamma}$. Evaluating the differential equation (2.2) with initial value $\tau(t=0)=\tau_0=0$ results in a stress

$$\tau(t) = \eta_0 \dot{\gamma} (1-e^{-t/\tau})$$  \hspace{1cm} (2.17)

and a viscosity which is independent of the shearrate $\dot{\gamma}$:

$$\eta = \eta_0 (1-e^{-t/\tau})$$  \hspace{1cm} (2.18)

This stress growth curve of the single Maxwell element is plotted in fig. 2.4.

2.2.4 Steady-state shear.

Fig. 2.4 illustrates that after a certain time of stress growth the stress will reach a constant value called the steady-state shear stress. The steady state shear behaviour is completely determined by the dashpot in the Maxwell model. As a consequence the steady state shear stress can be written as:

$$\tau = \eta_0 \dot{\gamma}$$  \hspace{1cm} (2.19)
2.3 Generalised Maxwell model.

The generalised Maxwell model consists of a finite number of Maxwell elements parallel as shown in fig. 2.5.

\[
\begin{align*}
\gamma & = \frac{\eta_{0i}}{G_{0i}} \\
\end{align*}
\]

(2.20)

The relaxation time \( \lambda_i \) of the \( i \)th Maxwell element is defined by

The constitutive equation for each Maxwell element is still of the form:

\[
\dot{\gamma} = \frac{\tau_i}{G_0} + \frac{\tau_i}{\eta_0} \\
\]

(2.21)

while the stress can be found by

\[
\tau = \sum_{i=1}^{n} \tau_i \\
\]

(2.22)
2.3.1 Stress relaxation.

In the case of the generalised Maxwell model the relaxation stress and the relaxation modulus are given by

\[ \tau(t) = \sum_{i=1}^{n} \tau_{\infty i} e^{-\frac{t}{\kappa_i}} \quad \text{with} \quad \tau_{\infty i} = G_{\infty i} \gamma_0 \]  

(2.23)

\[ G(t) = \sum_{i=1}^{n} G_{\infty i} e^{-\frac{t}{\kappa_i}} \]  

(2.24)

In fig. 2.6 the relaxation modulus is plotted and is again independent of shear \( \gamma_0 \). This figure visualises the contribution of each Maxwell element to the total relaxation modulus.

2.3.2 Dynamic behaviour.

The equations (2.5), (2.6), (2.7) and (2.8) are still valid for the generalised Maxwell model, but the storage- and loss modulus, the storage and loss viscosity and the phase shift now are:

\[ G'(\omega) = \sum_{i=1}^{n} \frac{G_{\infty i} \omega \lambda_i^2}{1+\omega^2 \lambda_i^2} \]  

(2.25)

\[ G''(\omega) = \sum_{i=1}^{n} \frac{G_{\infty i} \omega \lambda_i^2}{1+\omega^2 \lambda_i^2} \]  

(2.26)

\[ \eta'(\omega) = \sum_{i=1}^{n} \frac{G_{\infty i} \lambda_i}{1+\omega^2 \lambda_i^2} \]  

(2.27)

\[ \eta''(\omega) = \sum_{i=1}^{n} \frac{G_{\infty i} \omega \lambda_i^2}{1+\omega^2 \lambda_i^2} \]  

(2.28)
The dynamic modulus and viscosity are given by

\[ G''(\omega) = \sqrt{G''(\omega)^2 + G'''(\omega)^2} \]  

(2.30)

\[ \eta_d(\omega) = \sqrt{\eta'(\omega)^2 + \eta''(\omega)^2} \]  

(2.31)

The contribution of each Maxwell element to the total dynamic viscosity is illustrated in fig. 2.7.

**2.3.3 Stress growth.**

The stress growth for the generalised Maxwell model will be

\[ \tau(t) = \dot{\gamma} \sum_{i=1}^{n} \eta_{oi} (1 - e^{-\frac{t}{\lambda_i}}) \]  

(2.32)

\[ \eta = \sum_{i=1}^{n} \eta_{oi} (1 - e^{-\frac{t}{\lambda_i}}) \]  

(2.33)

This is visualised in fig 2.8.

**2.3.4 Steady-state shear.**

The steady state shear behaviour is completely determined by the dashpots

\[ \tau(t) = \dot{\gamma} \sum_{i=1}^{n} \eta_{oi} \]  

(2.33)
Chapter 3: Basic model suggested by Cox-Merz rule.

3.1 Introduction.

If a non-linear visco-elastic polymer melt is subjected to a sinusoidally varying deformation, the stress will also vary sinusoidally with a certain phase shift only if the deformation amplitudes are relative small. So for dynamic measurements with small strains - which is usually the case - the dynamic behaviour of the polymer melt is linear visco-elastic. Referring to chapter 2 this linear dynamic visco-elastic behaviour can be described with a generalised Maxwell model.

Polymer melts subjected to steady state shear will often show non-linear effects like shear-thinning which means that for increasing shear rates the steady-state viscosity will decrease. It’s obvious that this phenomenon can not be described with the generalised Maxwell model only predicting Newtonian behaviour (see eq. (2.33)), and as a consequence the empirical Cox-Merz relation given by (1.1) is not satisfied.

3.2 G-dashpot.

Suppose the linear dynamic behaviour of the polymer melt could be described with a single Maxwell element. To include the Cox-Merz relation the constitutive equation has to have a non-linear steady state behaviour that approximates the linear dynamic situation. This means that the shear rate dependence of the steady state viscosity \( \eta_s \) should be the same as the frequency dependence of the dynamic viscosity \( \eta_d \) of the single linear Maxwell element. For this reason a peculiar non-linear viscous element is introduced, the G-dashpot defined by

\[
\eta_s(\dot{\gamma}) = \frac{\eta_0}{\sqrt{1 + \dot{\gamma}^2 / \gamma_G^2}}
\]  

(3.1)

where \( \dot{\gamma}_0 \) and \( \eta_0 \) are the characteristic parameters. Comparing with fig. 2.3, fig. 3.1 shows that the shear rate dependence of the dashpot has an asymptotic behaviour similar to the frequency dependence of the dynamic viscosity \( \eta_d \) of a Maxwell element:
which implies that the G-dashpot will display Newtonian flow with viscosity \( \eta_0 \) at shear rates well below \( \dot{\gamma}_G \).

### 3.3 Modified Maxwell element.

Now the Maxwell element is modified by replacing the linear dashpot by the non-linear

\[
\dot{\gamma} \to 0 : \quad \eta_s(\dot{\gamma}) = \eta_0 \\
\dot{\gamma} \to \infty : \quad \eta_s(\dot{\gamma}) = \frac{\eta_0 \dot{\gamma}_G}{\dot{\gamma}}
\]

Fig. 3.2: Modified Maxwell element.

In appendix A has been deduced that the constitutive equation of this modified Maxwell element can be written as:

\[
\dot{\gamma} = \frac{\dot{\tau}}{G_0} + \dot{\gamma}_d \frac{\tau}{\sqrt{\eta_0 G - \tau^2}}
\]

The steady-state behaviour will completely be determined by the G-dashpot, but the main question is whether this non-linear element has a linear dynamic response for small deformations. The total dynamic response is determined by the combined conduct of the spring and the dashpot. It appears from appendix B that the dynamic behaviour of the G-dashpot is influenced by the magnitude of the amplitude \( \gamma_0 \) of the sinusoidal shear.
deformation. Fig. 3.3 clearly visualises that for decreasing shear amplitude the linear frequency independent area of the dashpot continues to higher frequencies. The asymptotes are

$$\omega \to 0 : \quad \eta_d = \eta_0$$  \hspace{1cm} (3.5)$$

$$\omega \to \infty : \quad \eta_d = \frac{\eta_0 \dot{\gamma}_o}{\gamma_o \omega}$$  \hspace{1cm} (3.6)$$

The dynamic behaviour of the linear spring is deduced in appendix C and illustrated in fig. 3.4: for increasing $G_o$ the asymptote $G_o/\omega$ shifts to higher frequencies. If the conduct of the spring and the dashpot are combined and the asymptote $G_o/\omega$ of the spring lies before the asymptotic line $\eta_d = \eta_0 \dot{\gamma}_o/\gamma_o \omega$ of the dashpot the dynamic behaviour of the total element will be completely linear (see fig. 3.5). The influence of the spring already starts at lower frequencies than the non-linearity of the dashpot resulting in a dynamic behaviour of the modified Maxwell element that corresponds with a linear Maxwell element. If $G_o/\omega$ lies behind $\eta_0 \dot{\gamma}_o/\gamma_o \omega$ non-linear dynamic effects do appear as illustrated in fig. 3.6 where for some shear amplitudes the resulting stresses are plotted. It’s clearly visible that for $\gamma_o > \eta_0 \dot{\gamma}_o/G_o$ (i.e. $G_o/\omega$ lies behind $\eta_0 \dot{\gamma}_o/\gamma_o \omega$) the stress 'deforms' with regard to the linear sinusoidal form.

3.4 Conditions for the Cox-Merz rule.

In the preceding pages it has been shown that for shear amplitudes $\gamma_o$ smaller than $\eta_0 \dot{\gamma}_o/G_o$ the dynamic behaviour of the modified Maxwell element is completely linear and resembles with the dynamic behaviour of a Maxwell element. To obey the Cox-Merz rule given by (1.1), the linear dynamic viscosity $\eta_d(\omega)$ has to match the non-linear steady state viscosity $\eta_0(\dot{\gamma})$ at $\omega=\dot{\gamma}$. This can be achieved by choosing the modulus of the spring $G_o$ in a way that the asymptotic lines $\eta_d(\omega)=G_o/\omega$ and $\eta_0(\dot{\gamma}=\omega)=\eta_0 \dot{\gamma}_o/\omega$ coincide being

$$G_o = \eta_0 \dot{\gamma}_o$$  \hspace{1cm} (3.7)$$

while the shear amplitude $\gamma_o$ has to be smaller than $\eta_0 \dot{\gamma}_o/G_o$, so smaller than 1 (i.e. 100%).
Substitution of eq. (3.7) into (3.1) leads to the following expression for the shear thinning behaviour of the G-dashpot.

\[ \eta_s = \frac{\eta_0}{\sqrt{1 + \dot{\gamma}^2 \lambda^2}} \]  

(3.8)

Since \( \eta_0 \) is related to \( G_0 \) and \( \lambda \) by eq. (2.1) the Cox-Merz version of the modified Maxwell element, further referred to as the G-element, is fully determined by the two parameters \( G_0 \) and \( \lambda \). The dynamic response of this specific modified Maxwell element will be completely linear at small shear amplitudes as the non-linearities of the dashpot shift to higher frequencies at shear amplitudes \( \gamma_0 \) smaller than 1. Consequently the frequency dependence of the dynamic viscosity of the G-element will be identical to the response of a linear Maxwell element.

As the shear rate dependence of the G-dashpot has been chosen mathematically identical to the frequency dependence of the dynamic viscosity \( \eta_d(\omega) \) of the linear Maxwell model, the Cox-Merz rule will be satisfied over the complete frequency range. This is demonstrated in fig. 3.7, where the dynamic viscosity of the G-element is compared with its steady state viscosity. The dynamic viscosity of the G-element presented in fig. 3.7 was obtained by numerical simulation of the dynamic experiment with shear amplitudes \( \gamma_0 = 0.01 \) (1%) and 0.1 (10%).

3.5 Generalisation.

In its generalised form the dynamic viscosity of the G-element is equal to the expression in eq. (2.31) derived from a generalisation of the linear Maxwell model. In steady-state shear flow the steady-state viscosity of the G-element can be expressed as:

\[ \eta_s = \sum_{i=1}^{n} \eta_i(\dot{\gamma}) = \sum_{i=1}^{n} \frac{\eta_{0i}}{\sqrt{1 + \dot{\gamma}^2 \lambda^2_i}} \]  

(3.9)

In comparing this expression with eq. (2.31) it is obvious that the generalised form of the
G-element, in contrast to the single element, does not mathematically obey the Cox-Merz rule. This deviation fundamentally originates from the fact that the dynamic viscosity $\eta_d$ of a generalised linear Maxwell model can not be regarded as the sum of the dynamic viscosities of the separate Maxwell elements, or

$$\eta_d(\omega) = \sqrt{\left[\sum_{i=1}^{n} \eta'_i(\omega)\right]^2 + \left[\sum_{i=1}^{n} \eta''_i(\omega)\right]^2} \approx \sum_{i=1}^{n} \sqrt{\eta'_i(\omega)^2 + \eta''_i(\omega)^2} \quad (3.10)$$

However the latter expression, often referred to as $\eta_{app}$, can be used as a useful upper approximation of the generalised dynamic viscosity and appears to be at most 25% larger than $\eta_d(\omega)$ of current polymer fluids [7]. Consequently the generalised G-model can be expected to show only slight deviations to the Cox-Merz rule.

### 3.6 Model verification.

To demonstrate the generalised G-element suggested in the previous section the model will be applied to a polymer melt displaying Cox-Merz behaviour: Low Density Polyethylene LDPE ('Melt I').

The linear dynamic behaviour of 'Melt I' was characterised by Laun by fitting of eight relaxation modes to the storage modulus [4]. The parameters $\lambda_i$ and $G_{oi}$ derived by Laun are listed in table 3.1. The linear characterisation in table 3.1 can easily be translated to the generalised G-model as introduction of $\lambda_i$ and $G_{oi}$ into eq. (3.7) directly defines the nonlinearity of the i th G-dashpot. The dynamic viscosity $\eta_d(\omega)$ of the G-model is identical to that of the linear Maxwell model stated in eq. (2.31). The steady state viscosity $\eta_s(\dot{\gamma})$ is expressed in eq. (3.9). In fig. 3.8 the dynamic viscosity $\eta_d(\omega=\dot{\gamma})$ and steady state viscosity $\eta_s(\dot{\gamma})$ of the G-model are compared with experimental data on the steady state viscosity of 'Melt I' [4]. In both figures the dynamic and steady state viscosity appear to be in good agreement with the experimental data. Moreover it is clear that the deviation between $\eta_d(\omega=\dot{\gamma})$ and $\eta_s(\dot{\gamma})$ is small.
3.7 Discussion.

It was shown that a slight modification of the linear Maxwell element being the introduction of a specific non-linear dashpot leads to a basic element which satisfies the Cox-Merz rule over the complete frequency range. This G-element could supply more insight in the physical origin of this analogon. Schulken et al. already expressed the opinion that the flexibility of the molecule is of influence on the correlation between steady state and dynamic data [5]. This influence can be recognised in eq. (3.7) where it is stated that the Cox-Merz equivalence can only occur in the case of a specific value of the elastic parameter $G_0$. 
Chapter 4: Non-linear visco-elastic behaviour modelled with a G-model.

4.1 Introduction.

In the preceding chapter a constitutive equation has been deduced approximately satisfying the Cox-Merz rule, based upon the G-element which consists of a linear spring and a non-linear G-dashpot acting in series. For the characterisation of a polymer melt satisfying the Cox-Merz rule, the material parameters of this non-linear constitutive model can be found by fitting the linear dynamic behaviour with a number of Maxwell elements. After the constitutive model has completely been embodied the model can be used to predict other flow situations. In this chapter stress growth and stress relaxation are computed with the G-model derived in paragraph 3.6 for the Low Density Poly-ethylene melt ('Melt I') and are compared with experimental results.

4.2 Stress growth of a single and generalised G-model.

At time $t=0$ the G-model is loaded with a constant shearrate $\dot{\gamma}$. The constitutive equation of the single G-element can be written as

$$\tilde{\tau} = G_0 \dot{\gamma} - G_0 \dot{\gamma} \frac{\tau}{\sqrt{\eta_0 \dot{\gamma}^2 - \dot{\gamma}^2}}$$  \hspace{1cm} (4.1)

with initial value

$$\tau(t=0) = 0$$  \hspace{1cm} (4.2)

In fig. 4.1 stress growth curves for $\dot{\gamma} = 0.01, 0.5, 1$ and 2 [1/sec] are plotted for the single G-element. Comparing with the curve of the single Maxwell element presented by the crosses shows that the viscosity computed with the G-element is shearrate dependent in contrary to the Maxwell model. The same applies to the generalised G-model as illustrated in fig. 4.2 clearly visualising the contribution of each element to the total viscosity. For small shearrates $\dot{\gamma}$, the G-model approximates the linear Maxwell model.
With the 8 modes G-model derived for 'Melt I' in paragraph 3.6 the stress growth curves have been computed and in fig. 4.3 compared with the experimental data [6]. The stress growth behaviour appears to be well predicted by the G-model for almost all shear rates. The experimental steady-state viscosity values have to agree with the data in fig. 3.8, which is not the case for $\dot{\gamma}=10$ so that the G-model does not fit for that shear rate. At the same time it is obvious that the overshoot in the stress growth curves is not predicted by the G-model.

4.3 Stress relaxation of a single and generalised G-model.

At time $t=0$ the G-model is subjected to a constant shear $\gamma_0$. Substitution of $\dot{\gamma}=0$ in eq. (3.4) results in the constitutive equation for the single G-element:

$$\dot{\tau} = -G_0\dot{\gamma}_G - \frac{\tau}{\sqrt{\eta_0\dot{\gamma}_G^2 - \tau^2}}$$

with initial value

$$\tau(t=0) = G_0\gamma_0$$

The initial value (4.4) plays a special part in this mathematical model. In appendix A has been shown that the stress of the modified Maxwell element is limited by a maximum absolute stress value

$$|\tau_{\text{max}}| = \eta_0\dot{\gamma}_G$$

Theoretically however the shear $\gamma_0$ can be any arbitrary value and so for a linear spring the initial value $\tau(t=0) = G_0\gamma_0$ can be greater than the maximum stress given by eq. (4.5). In the case of the G-element, being a special form of the modified Maxwell model, the limit value is reached for a shear $\gamma_0$:

$$\gamma_0 = \frac{\eta_0\dot{\gamma}_G}{G_0} = \frac{G_0}{G_0} = 1$$

19
For this reason a new initial value of differential equation (4.3) has to be introduced:

\[
\begin{align*}
\tau(t=0) &= G_0 \gamma_0 \quad \text{for} \quad \gamma_0 < 1 \\
\tau(t=0) &= G_0 \quad \text{for} \quad \gamma_0 = 1
\end{align*}
\]  
(4.7)

In fact this means that the linear spring is replaced by a particular spring being linear for \(\gamma_0 < 1\) and constant for \(\gamma_0 \geq 1\) as illustrated in fig. 4.4 and which is defined by

\[
\begin{align*}
\tau &= G_0 \gamma_s \quad \text{for} \quad \gamma_s < 1 \\
\tau &= G_0 \quad \text{for} \quad \gamma_s \geq 1
\end{align*}
\]  
(4.8)

This modification of the spring in the G-element does not affect the linear dynamic, the non-linear steady-state and the stress growth behaviour since the stress over the spring and over the dashpot are per definition equal which means that the limit stress will never be reached if the initial value is absolutely smaller than this limit. So if in the following pages a 'G-element' is mentioned the element with the G-dashpot and the spring defined by (4.8) is meant.

In fig. 4.5 the relaxation modulus of a single G-element is plotted for some shear values and compared with the relaxation modulus of a linear Maxwell element. In accordance with chapter 2 the relaxation modulus is defined as the quotient of the relaxation stress \(\tau(t)\) and the constant shear \(\gamma_0\)

\[
G(t) = \frac{\tau(t)}{\gamma_0}
\]  
(4.9)

The first striking difference with the linear Maxwell element is that the relaxation modulus \(G(t)\) predicted by the G-element is dependent of the shear \(\gamma_0\). For increasing \(\gamma_0\) the relaxation modulus \(G(t)\) decreases, while for a small shear value the relaxation curve approximates the linear Maxwell relaxation curve. This is completely caused by the non-linearity in the G-dashpot. At the same time it appears that the single G-element is not fully factorisable. However the generalised G-model turns out to be approximately factorisable as the relaxation curves in fig. 4.6 and fig. 4.7 can be vertically shifted over one another in the considered area. The relaxation curves in fig. 4.7 are computed with the 8 modes G-model deduced in paragraph 3.6 and are compared with experimental data [?].
For $\gamma_0=0.2$ the 8 modes G-model fit the experimental data very well but for increasing shear the vertical shifting is not similar to what is experimentally observed.
Chapter 5 : Conclusions and suggestions.

* By replacing the linear dashpot by a particular non-linear dashpot the Maxwell element can be modified into an element completely satisfying the empirical Cox-Merz rule over the complete frequency range if the modulus of the Hookean spring is related to the non-linearity of the dashpot. The generalised form of this G-model deviates at most 25% from the Cox-Merz rule.

* An 8 modes G-model has been deduced for 'Melt I'. The parameters of the constitutive equation have been found by fitting the linear dynamic behaviour with Maxwell elements. The Cox-Merz rule is well satisfied. However this 8 modes G-model does not predict the overshoot in the stress growth situation and the shear dependence of the relaxation modulus does not correspond with what is experimentally observed.

* It could be investigated how far a non-linearity in the spring affects the factorisibility and the shear dependence of the relaxation modulus of the single and generalised G-model.

* Further the G-model could be extended to a 3-D model to get insight in three dimensional stress situations which much more approximate the experimental reality.
References.

Figures and tables.

**Fig. 2.2**: Relaxation modulus of a single Maxwell element.
\[ \lambda = 4 \text{ [s]} \quad G_0 = 5000 \text{ [Pa]} \]

**Fig. 2.3**: Dynamic viscosity of a single Maxwell element.
\[ \lambda = 4 \text{ [s]} \quad G_0 = 5000 \text{ [Pa]} \]
Fig. 2.4: Stress growth of a single Maxwell element.

\[ \lambda = 4 \text{ [s]} \quad G_0 = 5000 \text{ [Pa]} \quad \dot{\gamma} = 1, 2, 4 \text{ [1/s]} \]

Fig. 2.6: Relaxation modulus of a generalised Maxwell model.

\[ \lambda = 10, 1, 0.1 \text{ [s]} \quad G_0 = 2000, 10000, 30000 \text{ [Pa]} \]
Generalised Maxwell model

Fig. 2.7: Dynamic viscosity of a generalised Maxwell model.
\[ \lambda = 10, 1, 0.1 \text{ [s]} \quad G_0 = 2000, 10000, 30000 \text{ [Pa]} \]

Fig. 2.8: Stress growth of a generalised Maxwell model.
\[ \lambda = 10, 1, 0.1 \text{ [s]} \quad G_0 = 2000, 10000, 30000 \text{ [Pa]} \]
Fig. 3.1: Steady-state viscosity of a G-dashpot.
\[ \eta_0 = 5000 \text{ [Pas]} \quad \dot{\gamma}_0 = 0.1 \text{ [1/s]} \]

Fig. 3.3: Dynamic viscosity of a G-dashpot.
\[ \eta_0 = 5000 \text{ [Pas]} \quad \dot{\gamma}_0 = 0.1 \text{ [1/s]} \]
\[ \gamma_0 = 10, 1, 0.1, 0.01 \text{ [-]} \]
Fig. 3.4: Dynamic viscosity of a linear spring.

\[ \eta_0 = 10, 100, 1000, 10000 \text{ [Pa]} \]

Fig. 3.5: Dynamic viscosity of a modified Maxwell element.

\[ \eta_0 = 5000 \text{ [Pas]} \quad \dot{\gamma}_0 = 0.1 \text{ [1/s]} \quad \gamma_0 = 0.01 \text{ [-]} \]

\[ G_0 = 100 \text{ [Pa]} \]
Fig. 3.6: Dynamic response of a modified Maxwell model.

\[ \eta_0 = 10000 \text{ [Pas]} \quad \dot{\gamma}_0 = 1 \text{ [1/s]} \quad G_0 = 20000 \text{ [Pa]} \]
\[ \omega = 1 \quad \gamma_0 = 2, 1, 0.6, 0.2, 0.05 \text{ [-]} \]

Fig. 3.7: Dynamic and steady-state viscosity of a G-element.

\[ G_0 = 300000 \text{ [Pa]} \quad \lambda = 0.01 \text{ [s]} \]
<table>
<thead>
<tr>
<th>i</th>
<th>$\lambda_i$ [s]</th>
<th>$G_{oi}$ [Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1 \cdot 10^3$</td>
<td>$1.00 \cdot 10^0$</td>
</tr>
<tr>
<td>2</td>
<td>$1 \cdot 10^2$</td>
<td>$1.80 \cdot 10^2$</td>
</tr>
<tr>
<td>3</td>
<td>$1 \cdot 10^1$</td>
<td>$1.89 \cdot 10^3$</td>
</tr>
<tr>
<td>4</td>
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<tr>
<td>7</td>
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<td>$9.48 \cdot 10^4$</td>
</tr>
<tr>
<td>8</td>
<td>$1 \cdot 10^{-4}$</td>
<td>$1.29 \cdot 10^5$</td>
</tr>
</tbody>
</table>

Table 3.1: Relaxation spectrum for 'Melt I' (Laun).

Fig. 3.8: Dynamic and steady-state viscosity of an 8 modes G-model for 'Melt I'.

$\lambda_p$, $G_{oi}$ see table 3.1

T=150 [°C]
Fig. 4.1: Stress growth of a single G-element.
\[ \lambda = 4 \, [s] \quad G_0 = 20000 \, [Pa] \quad \dot{\gamma} = 0.01, 0.5, 1, 2 \, [1/s] \]

Fig. 4.2: Stress growth of a generalised G-model.
\[ G_0 = 2000, 10000, 30000 \, [Pa] \quad \lambda = 10, 1, 0.1 \, [s] \]
Fig. 4.3: Stress growth of a 8 modes G-model for 'Melt I'.

\( \lambda_0, G_0 \) see table 3.1

Fig. 4.4: Special non-linear spring of the G-model.

\( G_0 = 1000 \) [Pa]
Fig. 4.5: Relaxation modulus of a single G-element.
\[ \lambda = 4 \text{ [s]} \quad G_0 = 5000 \text{ [Pa]} \quad \gamma_0 = 0.1, 0.5, 0.9, 1.5 \text{ [-]} \]

Fig. 4.6: Relaxation modulus of a generalised G-model.
\[ G_0 = 2000, 10000, 30000 \text{ [Pa]} \quad \gamma_0 = 10 \text{ [-]} \]
\[ \lambda = 10, 1, 0.1 \text{ [s]} \]
Fig. 4.7: Relaxation modulus of an 8 modes G-model for 'Melt I'.
\( \lambda_p \), \( G_{01} \) see table 3.1
Appendix A: Constitutive equation of the modified Maxwell element.

The modified Maxwell element consists of a linear spring and a non-linear dashpot acting in series as shown in fig. 3.2. This results in expressions for the stress $\tau$ of spring and the dashpot, for the shear $\gamma$ and the shearrate $\dot{\gamma}$.

\begin{align*}
\text{spring : } & \quad \tau = G_0 \gamma_s & \quad (A.1) \\
\text{dashpot : } & \quad \tau = \frac{\eta_0 \dot{\gamma}_d}{\sqrt{1 + \dot{\gamma}_d^2 / \dot{\gamma}_G^2}} & \quad (A.2) \\
\text{shear : } & \quad \gamma = \gamma_s + \gamma_d & \quad (A.3) \\
\text{shearrate : } & \quad \dot{\gamma} = \dot{\gamma}_s + \dot{\gamma}_d & \quad (A.4)
\end{align*}

Equation (A.1) can be written as

\[ \dot{\gamma}_s = \frac{\dot{\tau}}{G_0} \quad (A.5) \]

Transformation of (A.2) gives

\[ \dot{\gamma}_d^2 = \frac{\tau^2 \dot{\gamma}_G^2}{\eta_0^2 \dot{\gamma}_G^2 - \tau^2} \quad \text{with} \quad \eta_0^2 \dot{\gamma}_G^2 \neq \tau^2 \quad (A.6) \]

From eq. (A.2) can be deduced that

\[ \lim_{\gamma_s \to \infty} \frac{\eta_0 \dot{\gamma}_d}{\sqrt{1 + \dot{\gamma}_d^2 / \dot{\gamma}_G^2}} = \eta_0 \dot{\gamma}_G \quad (A.7) \]

\[ \lim_{\gamma_s \to -\infty} \frac{\eta_0 \dot{\gamma}_d}{\sqrt{1 + \dot{\gamma}_d^2 / \dot{\gamma}_G^2}} = -\eta_0 \dot{\gamma}_G \quad (A.8) \]
and therefore equation (A.6) can be written as

\[ \dot{\gamma}_d = \frac{\tau \dot{\gamma}_G}{\sqrt{\eta_0 \dot{\gamma}_G - \tau^2}} \]  

(Sub. 8.4)

Substitution of eq. (A.5) and (A.9) into (A.4) results in a constitutive equation for the modified Maxwell element given by:

\[ \dot{\gamma} = \frac{\dot{\tau}}{G_0} + \frac{\tau \dot{\gamma}_G}{\sqrt{\eta_0 \dot{\gamma}_G - \tau^2}} \]  

(Sub. 10)
Appendix B: Dynamic properties of the G-dashpot.

For linear visco-elastic material behaviour the dynamic viscosity is defined as

\[ \eta_d(\omega) = \frac{|\tau|}{|\dot{\gamma}|} \]  \hspace{1cm} (B.1)

where

|\tau| = \text{the modulus of the complex stress,}
|\dot{\gamma}| = \text{the modulus of the complex shearrate.}

Non-linear visco-elastic behaviour results in a periodically varying stress which is normally not sinusoidal and therefore leading to a time dependent argument and phaseshift of the complex stress.

\[ \eta_d(\omega, t) = \frac{|\tau|}{|\dot{\gamma}|} \]  \hspace{1cm} (B.2)

In the case that the non-linear visco-elastic behaviour results in a periodical stress resembling a deformed sinus, the place of the zeros remains the same compared with the linear situation (see fig. 3.6) and there will be still only one maximum between two neighbouring zeros. As a consequence a new dynamic viscosity can be defined as the quotient of the amplitude of the stress and the amplitude of the shearrate, which will be time independent for both the linear and the above mentioned peculiar form of non-linear behaviour.

\[ \eta_d(\omega) = \frac{\text{amplitude}(\tau)}{\text{amplitude}(\dot{\gamma})} \]  \hspace{1cm} (B.3)

This is used to demonstrate the dynamic behaviour of a pure viscous material modelled with a G-dashpot.
In general one can state for a purely viscous material that

\[ \tau = \tau(\dot{\gamma}) \]  

(B.4)

in the non-linear case resulting in a shearrate dependent steady state viscosity

\[ \eta_s(\dot{\gamma}) = \frac{\tau(\dot{\gamma})}{\dot{\gamma}} \]  

(B.5)

If pure viscous material is loaded with a sinusoidal strain

\[ \gamma(t) = \gamma_0 \sin(\omega t) \]  

(B.6)

the stress can be expressed as

\[ \tau(t) = \tau(\dot{\gamma}(t)) = \tau(\gamma_0 \omega \cos(\omega t)) \]  

(B.7)

If \( \tau(\dot{\gamma}) \) is a monotonically increasing function - which is physically realistic - the maximum stress will be reached at \( \cos(\omega t) = 1 \). For the dynamic viscosity defined by (B.3) yields

\[ \eta_d = \frac{\text{amplitude}(\tau)}{\text{amplitude}(\dot{\gamma})} = \frac{\tau(\gamma_0 \omega)}{\gamma_0 \omega} \]  

(B.8)

In comparing this expression with eq. (B.5) a specific interrelation between the dynamic viscosity and the steady-state viscosity is found

\[ \eta_d(\omega) = \eta_s(\dot{\gamma} = \gamma_0 \omega) \]  

(B.9)

indicating an equivalence between the shearrate and the multiplication of the strain amplitude \( \gamma_0 \) with the oscillation frequency \( \omega \).

This result is applied for the G-dashpot as shown in fig. 3.3 where the dynamic viscosity is plotted double logarithmically versus the oscillation frequency \( \omega \) for different values of \( \gamma_0 \). The frequency range where Newtonian, frequency independent, behaviour is observed clearly shifts to higher frequencies with decreasing strain amplitude \( \gamma_0 \). Only for a strain amplitude \( \gamma_0 = 1 \), the equivalence stated in eq. (B.9) is equal to the Cox-Merz interrelation given by (1.1).
Appendix C: Dynamic behaviour of a linear spring.

For linear visco-elastic behaviour the dynamic viscosity is defined as

\[ \eta_d(\omega) = \frac{|\tau|}{|\dot{\gamma}|} \]  \hspace{1cm} (C.1)

If a linear spring with stress-strain relation

\[ \tau = G_0 \gamma_s \]  \hspace{1cm} (C.2)

is subjected to

\[ \gamma_s = \gamma_0 \sin(\omega t) \]  \hspace{1cm} (C.3)

the modulus of the stress and the modulus of the shearrate can be expressed as

\[ |\tau| = G_0 \gamma_0 \]  \hspace{1cm} (C.4)

\[ |\dot{\gamma}_s| = \gamma_0 \omega \]  \hspace{1cm} (C.5)

resulting in

\[ \eta_d = \frac{G_0}{\omega} \]  \hspace{1cm} (C.6)

This dynamic behaviour is visualised in fig. 3.4.
Appendix D: Some numerical notes.

All the non-linear differential equations have been numerically solved by means of a fourth order Runge-Kutta algorithm [7]. Only the constitutive equation for the relaxation stress of a G-element (eq. (4.3)) could be analytically reduced to a non-linear algebraic equation given by

\[
\ln \left( \frac{-(x-1)+\sqrt{1-x^2}}{(x-1)+\sqrt{1-x^2}} \right) - \sqrt{1-x^2} = \frac{G_0 t}{\eta_0} + C
\]

with \( C = \ln \left( \frac{-(x_0-1)+\sqrt{1-x_0^2}}{(x_0-1)+\sqrt{1-x_0^2}} \right) - \sqrt{1-x_0^2} \) (D.1)

\[
x = \frac{\tau (t^*=t)}{\eta_0 \dot{\gamma}_G}
\]

\[
x_0 = \frac{\tau (t^*=0)}{\eta_0 \dot{\gamma}_G}
\]

Numerical solutions for the stress at certain times \( t \) have been determined by making use of the bisection method [7].