Towards an understanding of filled rubbers

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Large-Amplitude Oscillatory Shear (LAOS) has become an increasingly popular technique for studying the properties of rheologically complex fluids [59–63]. In this method, the sample experiences oscillatory shear at a strain amplitude \( \gamma_0 \). The frequency of the oscillation \( \omega \) is typically fixed, in which case the period of oscillation is \( 2\gamma_0 / \omega \).

For sufficiently small strains amplitude the response to the sinusoidal input is a linear combination of a sine and cosine of the input frequency, and the usual linear viscoelastic functions \( G' \) and \( G'' \) are obtained. Higher harmonics are observed at a sufficiently high strain amplitude, and the in- and out-of-phase components of the fundamental, which are still typically denoted \( G' \) and \( G'' \), respectively, will change in magnitude and phase [64, 65]. Typical behavior is shown in [60] for an aqueous solution of a xanthan gum, where the onset of non-linearity is observed at a strain amplitude about 0.15. The data are often represented as a Lissajous figure, in which stress is plotted versus strain over a cycle with time as a parameter, as shown in [30]. The Lissajous figure is an ellipse in the linear regime [30]; at higher strains amplitude the magnitude and phase angle of the fundamental change, while the deviation from an ellipse is caused by the appearance of higher harmonics.

The method is not new; it was employed as early as 1969 by Macdonald and co-workers [66] and has been used ever since. More recently, Cho and co-workers [28] showed how to isolate recoverable (elastic) and dissipative (viscous) portions of the nonlinear response, which greatly enhanced the utility of the technique. Their approach was extended by Ewoldt and co-workers [29, 30] to incorporate Chebychev functions to characterize the complete stress-strain cycle; the Chebychev formulation is commonly employed today [67, 68]. LAOS appears to provide useful insight into material behavior [69–71] and it is straightforward to implement on conventional rheometers, especially with the availability of the MITlaos software [29]. It is often overlooked, however, that because the measurement within a single oscillation cycle is transient, and because LAOS operates by definition in a nonlinear regime, the effect of prior deformation history may influence the outcome of the measurement, and it is not clear to what extent the result corresponds to a useful material property. We consider two aspects of the nonlinear response in this work. One, which may seem to be paradoxical, is how to separate strain softening and strain hardening behavior in the nonlinear regime. The
other is to investigate the collapse of any aspect of the nonlinear behavior onto master curves from which general conclusions may follow [72–74].

5.1 MATERIALS AND METHODS

Our primary interest is in filled rubbers, where the large strain amplitude elasticity affects properties like the rolling resistance. We therefore studied one filled rubber and the two model systems introduced in the Chapter 2 (xanthan gum and hair gel). $G'$ and $G''$ as functions of the strain amplitude at a frequency of $\omega = 6.28 \text{ rad.s}^{-1}$ are shown in Figs. 5.1(A), (D) and (E) for the three systems, and the linear viscoelastic functions $G'(\omega)$ and $G''(\omega)$ are shown in Figs. 5.2 (A), (B) and (C).

Oscillatory measurements were carried out on an Anton Paar Physica MCR 300 rheometer with a plate-plate geometry. The plate-plate geometry was selected despite the non-homogeneous shear rate field, because the toughness of the filled rubbers precludes them being studied at room temperature in a cone-and-plate geometry. For the filled rubbers the plate diameter was 5 mm and the samples were disks with a thickness about 2.5 mm glued to the plates with a Loctite glue to avoid wall slip [23]. For the xanthan gum and the commercial hair gel the plate diameter was 50 mm and the gap 2 mm. The plates for the xanthan and hair gel were roughened to prevent wall slip. Shear banding is sometimes a concern in a plate-plate geometry, but no evidence of this phenomenon has been found in the range of strains or shear rates at which we are operating as observed by Coussot et al. [75]. All experiments reported in the present work were carried out at ambient temperature.

5.2 LAOS ANALYSIS

In this section we will define the parameters necessary to describe the LAOS experiments and then connect the strain sweeps and the strain versus stress experiments.

5.2.1 Stress, elastic stress and viscous stress

A sinusoidal strain excitation was imposed on the sample, and the stress response was measured; if the stress is plotted as a function of the measured strain, one obtains a Lissajous curve that generally has a roughly elliptical shape (non-sinusoidal strain cycles are discussed by Klein and coworkers [76]). In a classical, linear viscoelastic
measurement the storage and loss moduli are obtained from the equation for the stress as

\[ \sigma(t) = G'\gamma(t) + G''\dot{\gamma}(t)/\omega, \]  

(5.1)

where \(\sigma\), \(\gamma\), \(\dot{\gamma}\) and \(\omega\) are, respectively, the stress, strain, strain rate, and frequency of oscillation; \(G'\) and \(G''\) are the storage and loss moduli, respectively. This separation of the stress into viscous (dissipative) and elastic (recoverable) parts can be generalized to the non-linear case, whereby the stress signal is written as

\[ \sigma(t) = \frac{\sigma(t) + \sigma(-t)}{2} + \frac{\sigma(t) - \sigma(-t)}{2}. \]  

(5.2)

Cho and co-workers [28] have shown that the odd and even parts of Eq. (5.2) can be identified respectively as the elastic and the viscous stress (\(\sigma_e\) and \(\sigma_v\) afterwards) responses.

5.2.2 Chebychev analysis of the stress versus strain experiments

The considerations in [28] have been led further by Ewoldt et al. [29], who described the response within an oscillation cycle by a sum of Chebychev polynomial of the first kind denoted \(T_n\):

\[ \sigma(t) = \sum_{n \text{ odd}} \gamma_0(e_n(\gamma_0, \omega)T_n(\sin \omega t) + v_n(\gamma_0, \omega)\omega T_n(\sin \omega t)). \]  

(5.3)

In the linear regime only the \(n = 1\) terms remain and the expansion reduces to Eq. (5.1), with \(e_1\) and \(v_1\) correspond to \(G'\) and \(G''/\omega\), respectively. If higher harmonics are present, the Lissajous curve is no longer an ellipse. The MItlaos software [29] reports \(e_1\) and \(v_1\omega\) as \(G'\) and \(G''\), respectively, even in the nonlinear regime, and we adopt this convention here.

Figure 5.1(A) shows \(G'\) and \(G''\) at \(\omega=6.28 \text{ rad.s}^{-1}\) as a function of the strain amplitude \(\gamma_0\) for a 4% wt xanthan gum solution. The linear regime extends to a strain amplitude of approximately 0.15, with measured moduli in the linear regime of \(G'=365\ \text{ Pa}\) and \(G''=55\ \text{ Pa}\). Figure 5.1(B) shows a Lissajous curve in the linear regime, which is an ellipse that is described by Eq. (5.1), or equivalently Eq. (5.3) truncated at \(n = 1\).
Figure 5.1: LAOS measurements at a frequency of $\omega = 6.28 \text{ rad.s}^{-1}$. (A) Storage and loss moduli of a 4% wt Xanthan gum in water as functions of strain amplitude. (B,C): Lissajous curves for the Xanthan gum from LAOS strain sweeps with strain amplitudes of (B) 0.04 and (C) 1.0. The line in (B) corresponds to a fit to Eq. (5.1) with $G' = 365 \text{ Pa}$ and $G'' = 55 \text{ Pa}$. The line in (C) is a fit using Eq. (5.3) truncated at $n = 3$. (D,E): Storage and loss moduli as functions of strain amplitude for (D) filled SBR and (E) hair gel.
5.3 THE STRAIN SOFTENING/STRAIN HARDENING ISSUE

5.3.1 Statement of the problem

We now consider the non-linear regime. Figure 5.1 shows that the elastic modulus $G'$ decreases beyond the linear regime (also called the Payne effect [17, 18]) for all three materials, and from this measurement one thus concludes that the materials are strain softening. Fig. 5.1(B,C) shows an explicit example of a Lissajous curve in this strain regime, for $\gamma_0 = 1.0$, which is clearly no longer a simple ellipse, so higher order terms in the Chebychev expansion are required. As shown in Fig. 5.1(C), the data for the xanthan solution are adequately described by retaining terms only through $n = 3$ (i.e., two terms), and truncation at $n = 3$ turns out to describe all data for the rubber and hair gel as well. In the following, we will primarily focus for simplicity on the elastic part of the response, but the full sets of data for $e_3$ and $\nu_3 \omega$ relative to $G'$ and $G''$, respectively,
are shown in Fig. 5.3 as functions of the strain amplitude. As can be seen in Fig. 5.3(B), $v_3\omega$ is negligible compared to $G''$ for the filled rubbers.

For the elastic response, the main feature is that the elastic part of the stress-strain curve is no longer a straight line, but rather it curves upward at large strains, as shown in Fig. 5.4. This upturn is often viewed as an indication of strain hardening [29, 70]; the leading higher-order term in the Chebychev formulation, $e_3$, is indeed positive at large strains. We therefore need to confront the apparent paradox that the same data can be interpreted as indicating both strain softening and strain hardening.

![Figure 5.3: Ratio of the third harmonic to the first versus strain amplitude for the (A) elastic and (B) viscous stresses.](image)

**5.3.2 Different definitions of the modulus**

This issue is not new and has been already raised by Ewoldt et al. [29], but contrary to our present approach, which addresses the overall mechanical behavior of the systems, they focus on the local behavior represented by the Lissajous curves. To address this question, we have to consider what the different measurements tell us. Figure 5.4 shows the different ways in which an effective modulus can be defined from a single oscillation measurement, all of which have been used in the literature to characterize the material properties:

- $G'_M = \left. \frac{d\sigma}{dy} \right|_{y=0} = \left. \frac{d\sigma_e}{dy} \right|_{y=0}$ is the local slope at zero strain of both the elastic stress and the total stress.
- $G'_L = \left. \frac{\sigma}{y} \right|_{y=y_0}$ is the large strain elasticity, which interpolates between the two extrema of the elastic stress.
• $G' = \frac{\omega}{\pi \gamma_0} \int dt \sigma_e(t) \gamma(t)$ is the storage modulus as reported by the rheometer software, and is equal to $e_1[29]$.

For an expansion truncated at $n=3$, $G' = e_1, G'_M = G' - 3e_3$, and $G'_L = G' + e_3$.

![Graph](image)

Figure 5.4: Elastic stress (thin full line) and viscous stress (dashed line) versus strain for the same strain amplitude, with the definitions of the various elastic moduli

Table 5.1 gives the moduli from the xanthan solution data displayed in Figs. 5.1 (B) and (C). In the linear regime (strain amplitude of 0.04) all three definitions of a modulus give an identical value number. In the non-linear case, these parameters differ considerably, and the apparent intra-cycle strain hardening is expressed by the higher value of $G'_L$ (elasticity at high strains) relative to $G'_M$ (elasticity at low strains). The values of $e_1$ and $e_3$ are obtained from the fit to the Lissajous figure and are consistent with the independent measurements of the moduli.

<table>
<thead>
<tr>
<th>Strain amplitude</th>
<th>$G'(\text{Pa})$</th>
<th>$G'_L(\text{Pa})$</th>
<th>$G'_M (\text{Pa})$</th>
<th>$e_1(\text{Pa})$</th>
<th>$e_3(\text{Pa})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_0 = 0.04$</td>
<td>365</td>
<td>365</td>
<td>365</td>
<td>365</td>
<td>0</td>
</tr>
<tr>
<td>$\gamma_0 = 1.0$</td>
<td>87.4</td>
<td>107.8</td>
<td>27.4</td>
<td>87.4</td>
<td>20.4</td>
</tr>
</tbody>
</table>

Table 5.1: Values of the elastic parameters computed from the data in Figures 5.1 (B) and (C).

The three systems examined here demonstrate qualitatively very similar behavior; it is evident from the strain sweeps in Figs. 5.1 (A), (D), and (E) that these systems are all strain softening, while the positive value of $e_3$ at large strain for each system again seems to imply strain hardening.
5.3.3 Resolution

Figure 5.5: Elastic stress at $\omega = 6.28 \text{ rad s}^{-1}$ for different strain amplitudes: (A) xanthan gum, (B) filled SBR, and (C) hair gel.

The solution to the apparent paradox is contained in Fig. 5.5, where the elastic stress for each system is plotted as a function of strain for different strain amplitudes. The strain softening is clearly visible as the change in slope of the stress-strain curve at zero strain: this is by far the dominant effect, and the system is therefore strain softening. The apparent strain hardening that comes from the LAOS analysis is mostly visible on the curve for the largest strain amplitude as a slight upturn at high strain. In fact, it follows from the Chebychev expansion that the elastic stress-strain dependence in the LAOS analysis through $n = 3$ can be written as:

$$\sigma_e(t) = G_M' \gamma + 4e_3 \frac{\gamma^3}{\gamma_0^3}$$  \hspace{1cm} (5.4)

As is evident from the figure, the decrease in the modulus $G_M'$ is much more important than the correction due to $e_3$, hence a strain hardening conclusion from the LAOS
Lost in LAOS

analysis is misleading regarding the overall mechanics. \( \frac{d\sigma_e}{dt} = G'_M + 12\varepsilon_3 \gamma^2 / \gamma_0^2 \) is often called a tangent modulus, and a tangent modulus that increases with increasing strain indicates local strain hardening, but the overall behavior is strain softening. Hence, the strain sweep of the modulus is the reliable indicator of strain hardening or softening, since the intra-cycle measurement shows only local behavior. Very recently, Ewoldt and Bharadwaj [77] arrived at a similar conclusion, namely that there is a fundamental difference between inter- and intracycle behavior. They quantify the correction to the average modulus as \( \varepsilon_1 \) and the higher harmonics as \( \varepsilon_3 \); it is clear (from their Fig. 5.7, for example) that these terms can have the same or opposite signs.

5.4 FOCUS ON THE STRAIN SOFTENING

Now that we have clarified this issue, we focus on the observed strain softening. We will first investigate why \( G'_M \) depends on the strain amplitude and then study the nature of the strain dependence of the strain softening.

5.4.1 \( \gamma_0 \) dependence of \( G'_M \)

Before going further we need to understand why \( G'_M \) depends on the strain amplitude (Fig. 5.5). This is simply the strain softening and is unexpected: whether a material is sheared to 0.1 or 1 times the strain amplitude, the behavior at low strains must be the same.

In this respect it is important to note that the LAOS cyclic measurements discussed so far reflect the dynamic steady state that is reached after initial transients have disappeared, and that they are averages over multiple cycles in order to obtain good resolution. The first cycle is inherently different from subsequent cycles, since the system does not “know” what the strain amplitude will be. The slope of the stress-strain curve at the origin will therefore change over the course of the first cycle(s) prior to reaching the steady-state value \( G'_M \); the slope on the first cycle should correspond to the linear viscoelastic value of \( G' \). Figure 5.6 shows the first two cycles for the filled SBR at two different strain amplitudes, and it is clear that the stress-strain behavior is the same over the first cycle until the smaller strain amplitude is reached. The initial slope at the origin is indeed equal to the value of \( G' \) obtained in the linear viscoelastic measurement, while the smaller slope on the second cycle on passing through zero strain is indicative of the effect of memory and the strain softening.
Figure 5.6: Full Lissajous curves for two different strain amplitudes, with two complete cycles displayed for each $\gamma_0$. The cycles are obtained by a succession of rotation experiments, with the constant shear rate $\gamma(t) = 10^{-4} \text{ s}^{-1}$ for all cycles.

5.4.2 Nature of the dependence of the strain softening on strain and frequency

Now, the remaining question regarding the strain softening is the nature of the dependence of $G'_M$ (or, neglecting $e_3$, simply $G'$) on the strain amplitude. It turns out that two parameters are important: the product $\gamma_0 \omega$, where $\gamma_0$ and $\omega$ are the strain amplitude and the frequency, respectively, and the strain amplitude itself. We refer to $\gamma_0 \omega$ henceforth as the maximum shear rate. The effect of the maximum shear rate can easily be quantified by comparing measurements carried out at constant values of $\gamma_0 \omega$ from $10^{-4}$ to $5 \times 10^{-1} \text{ rad s}^{-1}$, as shown in Fig. 5.7(A) for the SBR. Here, the frequency and the strain amplitude were varied simultaneously along each curve to keep $\gamma_0 \omega$ constant, so that each set of symbols corresponds to a single maximum shear rate. Clearly, the curves for different $\gamma_0 \omega$ are different, showing that the value of the modulus depends on the maximum shear rate. The curves appear to be parallel, however, and the data can be superimposed onto single master curves for both $G'$ and $G''$ by shifting horizontally along the frequency axis by a shift factor that is essentially the maximum shear rate, as shown in Figs. 5.7(B), (C), and (D) for the filled SBR, xanthan gum and hair gel, respectively. The superposition is least satisfactory for $G''$ of the hair gel at small strains, where there is a notable frequency dependence. Hence, the dominant time scale in the non-linear regime is the one imposed by the frequency of oscillation (time scale $2\pi/\omega$)[74] and the shifted variable is essentially the inverse of the strain amplitude. The same scaling of the data for the third harmonic of the elastic stress can be obtained as in [73].

We can consider three different cyclic experiments to measure the storage modulus:
Figure 5.7: (A) Storage modulus of the filled SBR versus frequency for maximum shear rates $\gamma_0 \omega$ varying from $10^{-4}$ rad.s$^{-1}$ to $5 \times 10^{-1}$ rad s$^{-1}$. Each curve corresponds to a fixed maximum shear rate. Rescaled storage and loss moduli by shifting the data for (B) the filled SBR, (C) the xanthan gum and (D) the hair gel.

- Strain sweep at a constant frequency.
- Frequency sweep at constant strain amplitude.
- Strain or frequency sweep at constant maximum shear rate.

One needs to ask whether these experiments are equivalent, which we do by considering the rescaling discussed above. For the hair gel, shown in Fig. 5.8(A), the data from the different cycles clearly lie on the same curve when plotted versus reciprocal strain amplitude. For the filled SBR and the xanthan gum (Figs. 5.8(B) and (C), respectively), on the other hand, the frequency sweep and strain sweep data deviate from the master curve developed from the constant maximum shear rate measurements, especially at small strain amplitudes in the case of the filled rubber. This is a reflection of the frequency dependence of $G'$ for the rubber in the linear regime, as shown in Fig. 5.2(B);
Figure 5.8: Superposition of strain sweeps at constant frequency (full line, \( \omega = 6.28 \text{ rad.s}^{-1} \); dashed line \( \omega = 62.8 \text{ rad.s}^{-1} \)), strain sweeps at constant maximum shear rates (squares), and frequency sweeps at constant strain amplitudes (indicated by arrows and rectangles in (a), \( 0.068 \leq \omega \leq 6.28 \text{ rad.s}^{-1} \)). (A) hair gel, (B) filled SBR, and (C) xanthan gum.

The linear modulus for the hair gel, shown in the Fig. 5.2(C), is independent of frequency. The existence of the master curve in the nonlinear regime for the rubber is significant, because it indicates that \( G' \) depends only on strain amplitude and not on rate for finite strains, which can be important in applications involving cyclic loads. In the case of xanthan gum (Fig. 5.8(C)), the frequency dependence also leads to a deviation in the strain softening regime. We have rescaled the xanthan gum data in Fig. 5.9 including the frequency dependence of \( G' \) in the strain softening regime in the shift factor. The superposition of the strain sweep, frequency sweeps and constant maximum shear rate experiments is now considerably improved. The timescale imposed by the forcing frequency thus remains dominant, but there is a contribution from the intrinsic relaxation modes of the materials as well.
Figure 5.9: Superposition of strain sweeps at constant frequency (full line, $\omega=6.28 \text{ rad.s}^{-1}$; dashed line, $\omega=62.8 \text{ rad s}^{-1}$), strain sweeps at constant maximum shear rates (squares), and frequency sweeps at constant strain amplitudes (as in Fig. 5.8, $0.068 \leq \omega \leq 6.28 \text{ rad.s}^{-1}$) for the xanthan gum plotted versus the inverse of the strain amplitude times the frequency multiplied by the frequency dependence of the linear viscoelastic response.

CONCLUSION

The main aim of this chapter has been to elucidate the connection between the usual nonlinear viscoelastic measurements and the Lissajous/LAOS analysis of the same materials. Perhaps surprisingly, we show here for three very different systems that the conclusions from two common ways of analyzing the same data appear to be contradictory: from a regular strain sweep one concludes that the materials are strain softening, whereas the LAOS analysis of a single oscillation cycle indicates strain hardening. We show here that the materials are indeed strain softening, and that the apparent strain hardening that follows from the LAOS analysis is a consequence of the use of a tangent modulus and is a local effect. We subsequently focus on understanding the strain softening, notably the observation that the amplitude depends on the rate at which the deformation is applied. We propose a rescaling that allows us to superimpose the data for both the elastic and loss moduli from different types of oscillation measurements: strain sweeps, frequency sweeps, and constant maximum shear rate experiments. The conclusion from the rescaling is that the dominant timescale for the three systems is the one imposed by the deformation rate in the experiment, not an intrinsic time scale: the rearrangements in the material are due to the applied stress or strain amplitude, and the strain softening is a consequence thereof.