Characterization of the structure at rest in foods
(Example: Ketchup)

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3 Summary

1 Introduction

The following information about the rheological behavior of foods is important for practical applications:

(1) Consistency or structural strength at rest
Practical application:
Stability of dispersions or gels, long-term storage stability, separation or sedimentation behavior, characterization of the structure at rest (as a viscoelastic solid or liquid), “yield point”

(2) Flow behavior
Practical application:
Processability, behavior when filling into containers, sensation in the mouth, “viscosity”

(3) Time-dependent behavior immediately after a sudden change in shear conditions.
Practical application:
Structural decomposition and regeneration, leveling or sagging behavior of pastes, creams, gels, and all kind of dispersions, after filling in and taking out of the container (bottle, tube, etc.), layer thickness of coatings, “thixotropic behavior”

This report focuses on topic (1) and briefly mentions topics (2) and (3). The discussed testing and analysis methods are presented as test results of three different ketchup samples. All the tests were carried out at a test temperature of $T = +20$ °C, using a Physica MCR 300 rheometer with cylinder measuring systems (MS CC). Thanks to Petra Boudaoua for performing the tests.
2 Evaluation of the structure at rest using rotational tests

2.1 Classic yield point determination
2.1.1 Settings as a shear stress ramp

The “classic yield point test” is carried out as a flow curve test. Usually a shear stress ramp is preset with increasing shear load (Fig.1).

Fig. 1: Settings for a controlled shear stress ramp

2.1.2 Determining the yield point from a flow curve

The term “apparent yield point” is sometimes used to indicate that the yield point is not a constant value but a value that depends on the test and analysis conditions. Nevertheless, this value is usually sufficient for simple quality control tests.

When the flow curve, i.e. the $\gamma$-$\tau$ function, is represented in a diagram on a linear scale, the yield point $\tau_y$ can be seen as the intersection on the $\tau$ axis (Fig. 2). Yield point values which are determined in different laboratories often lead to endless and frustrating discussions because the values do not correspond. The following comments will help explain this:

- **Yield points are not material constants!**
  
  In the “classic” yield point measuring method with preset shear stress ramp, the yield point is determined as the highest shear stress value at which the rheometer still detects no movement. The yield point is exceeded after detecting the first speed $n > 0$.
  
  That means: the yield point as a test result depends on the resolution of the rheometer for the lowest speed $n_{min}$. In other words: The more sensitive the rheometer, the lower the speed it can detect and therefore the lower is the resulting yield point value. A high-performance rheometer will therefore give lower values for the yield point than a less powerful rheometer.
  
  Conclusion: Yield point tests which are carried out on the same sample with different instruments, can result in different results. Yield point values are therefore relative values which depend greatly on the capability of the rheometer.

- **Yield points are time-dependent!**
  
  Yield points depend on the test conditions because for most samples, the shorter the preset ramp time or measuring point duration, the higher the determined yield point value.
  
  The reason for this behavior: some interaction forces between the components of the sample only gradually yield under shear load and this happens over a certain period of time. Even applying a constantly high shear stress, the internal network of forces can often resist the load only for a certain period of time before it begins to yield.

Often the yield point is determined in tests presetting a shear rate ramp (instead of a shear stress ramp). Using approximation functions (regression models), the apparent yield point can be calculated then by a software analysis program (e.g. as yield point according to the Bingham, Casson, Herschel/Bulkley, Windhab or polynomial model).
2.1.3 Test results: Flow curves

In diagrams with a linear scale, above all the high values of the represented curve functions are clearly to be seen (Fig. 4). In order to show also the lower values, it is better to use a logarithmic scale presenting both low and high values with the same priority (Figs. 3 and 5).

Looking at a log/log diagram makes it clear that a yield point value is not a material constant. The curve in Fig. 5 starts at the shear rate $\dot{\gamma} = 0.1 \, \text{1/s}$. This is the speed value which lies nearest to the shear rate value zero and is therefore taken as the value for the yield point in this analysis. However, a higher $\tau$ value would be determined as yield point if the rheometer’s measuring range would be more limited, therefore detecting shear rates e.g. not below $\dot{\gamma} = 1 \, \text{1/s}$. Or, a lower yield point value would result if the flow curve could be measured down to lower shear rates; as the $\tau$ curves in Fig. 5 would still continue showing a certain slope to the lower left.

From Fig. 5 we obtain the following “yield points” as shear stress values at the shear rate $\dot{\gamma} = 0.1 \, \text{1/s}$:

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>11 Pa</td>
<td>12 Pa</td>
<td>7 Pa</td>
</tr>
</tbody>
</table>

Fig. 4:
Flow curves of the three ketchup samples, diagram with a double linear scale

Fig. 5:
Flow curves of the three ketchup samples, diagram with a double logarithmic scale
2.2 Yield point between the elastic and viscous deformation range

2.2.1 Determining the yield point using the tangent crossover method

In many dispersions and gel-like or paste-like materials below the yield point, an elastic deformation \( \gamma \) already occurs at the lowest shear stress value. In this deformation range, the investigated sample can be seen as a soft elastic solid which behaves according to Hooke’s law. This law formulates elastic behavior as
\[
G = \frac{\tau}{\gamma},
\]
with the shear modulus \( G \) [Pa].

The points in Fig. 6 show the individual measuring points, and the lines are the tangents which are positioned on the two branches of the curve function. Here, the yield point is defined as the crossover point of the two tangents. Below the yield point, i.e. at the lowest shear stress and deformation values, the elastic behavior of the sample can be seen in the form of a constant slope of the curve. Here, the proportionality of \( \gamma \) and \( \tau \) can be seen (Hooke’s law).

Please note: Yield point values are often difficult to reproduce using the tangent crossover method (with one tangent through the low deformation and another through the high deformation values). The reason for this is that the second part of the measuring curve (at high shear rates) is rarely a curve function with a constant slope in the \( \lg \tau - \lg \gamma \) diagram. It is therefore often difficult to set a tangent through the data points on this part of the measuring curve.

Fig. 6: Determining the yield point using the tangent crossover method.

2.2.2 Yield zone instead of yield point

When working with the tangent crossover method, it is assumed that the internal structures of the investigated substance almost all break down at one point under a certain shear load. In reality, the internal structural strength usually decreases gradually within a fairly wide transition range. Therefore, it is sometimes better to refer to this range as a yield zone or yield transition zone, and not as a single yield point.
2.2.3 Test results: Yield point as the limit of the elastic deformation range

In order to determine the limit of the range of “shear-at-rest”, it is useful to take the yield point as the shear stress value at which the range of elastic or reversible deformation behavior is exceeded. With a further increase of the shear load, some irreversible deformation occurs in the material (i.e. deformation which remains after the shear load is removed, and thus, “inelastic” behavior).

From Fig. 7 we obtain the following yield points as the upper limit of the elastic range:

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 Pa</td>
<td>4 Pa</td>
<td>5 Pa</td>
</tr>
</tbody>
</table>

With this analysis method, a tangent is positioned on the lower left part of the measuring curve. In this range, the $\log_{10}\tau - \log_{10}\gamma$ curve displays a constant slope. The last point in the linearly increasing $\log_{10}\tau - \log_{10}\gamma$ curve (in the lower left of the diagram) is taken as the limit of the linear elastic deformation range. The yield point value $\tau_y$ is the limiting shear stress value at which the curve deviates from the tangent or deviates from the permitted bandwidth preset by the user in the analysis software.

Fig. 7: Double logarithmic $\log_{10}\tau - \log_{10}\gamma$ diagram of the three ketchup samples
3 Evaluation of the structure at rest using oscillatory tests

3.1 Amplitude sweeps

3.1.1 Settings

The oscillation amplitude is varied at a constant oscillation frequency (Fig 8; e.g. with the angular frequency \( \omega = 10 \text{ 1/s} \)).

Fig. 8: Settings for the amplitude sweep, here with preset deformation

3.1.2 Test results: Amplitude sweeps

The amplitude sweep should achieve the following three aims:

- Determination of the limit \( \gamma_L \) of the linear viscoelastic range (LVE range). The limit of this range is exceeded at the point at which the first of the two curves (\( G' \) or \( G'' \) function) begins to leave the constant plateau value significantly (e.g. showing a decreasing \( G' \) value). The permitted bandwidth can be defined by the user, e.g. as 5 or 10% maximum deviation.
- Characterization of the material structure: Does the sample show gel character with \( G' > G'' \) or liquid character with \( G'' > G' \)? All the three ketchup samples from Fig. 9 show \( G' > G'' \) in the LVE range, which means they all have gel character at very low deformation.
- Evaluation of the structural strength as the \( G' \) value in the LVE range (sometimes called “rigidity”).

![Graph of amplitude sweeps](image)

Fig. 9: Amplitude sweeps of the three ketchup samples (all determined at \( \omega = 10 \text{ 1/s} = \text{constant} \)). The storage modulus \( G' \) (elastic behavior) and loss modulus \( G'' \) (viscous behavior) curves are shown as a function of the deformation \( \gamma \).
Amplitude sweeps (AS) can also be presented over the shear stress $\tau$. The yield point $\tau_y$ is reached when the curve of $G'(\tau)$ or $G''(\tau)$ begins to decrease significantly. As an alternative, this can be displayed using the loss factor $\tan \delta = G''/G'$ (see Fig. 10): The yield point $\tau_y$ is reached when the $\tan \delta$ value increases significantly, e.g. when the ratio value between viscous and elastic behavior increases clearly, and thus, the liquid character becomes increasingly dominant.

![Amplitude sweeps of the three ketchup samples](image)

Fig. 10: Amplitude sweeps of the three ketchup samples. To analyze the yield point, the curves of the loss factor $\tan \delta$ are shown as a function of the shear stress $\tau$.

For the evaluation, a tangent is positioned on the lower left part of the measuring curve. In this range, the $\tan \delta$ curve shows an approximately constant plateau value. As yield point $\tau_y$ is taken the limiting value of the shear stress at which the measuring curve deviates from the horizontal course or leaves the permitted bandwidth defined by the user in the software. The larger points shown in the diagram (Fig. 10) are the points determined as the yield points by the software analysis program.

From Fig. 9 we obtain the structural strength $G'$ (in the LVE range) as well as the limiting value of the LVE range $\gamma_L$ (concerning the deformation), and from Fig. 10 we obtain the following three yield points $\tau_y$:

<table>
<thead>
<tr>
<th></th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G'$ [Pa]</td>
<td>600</td>
<td>200</td>
<td>320</td>
</tr>
<tr>
<td>$\gamma_L$ [%]</td>
<td>0.5</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>$\tau_y$ [Pa]</td>
<td>10</td>
<td>3</td>
<td>5</td>
</tr>
</tbody>
</table>
3.2 Frequency sweeps

3.2.1 Settings

The oscillation frequency is varied at a constant oscillation amplitude (Fig. 11; with the deformation amplitude $\gamma_A$). It should be selected: $\gamma_A \leq \gamma_L$, with $\gamma_L$ as the limiting value of the LVE range (see Chapter 3.1.2). Yield points are often determined in order to estimate the sample’s long-term stability in storage. Although the frequency sweep (FS) does not measure the yield point as a shear stress value, the test is very useful for investigating long-term applications, and it can give application relevant results on the subject of long-term storability.

Fig. 11: Settings for the frequency sweep, here with preset deformation

3.2.2 Test results: Frequency sweeps

Frequency sweeps (FS) can be used to evaluate time-dependent rheological behavior. Low frequencies simulate long-term effects or slow movements, and high frequencies simulate short-term effects or fast movements. In order to analyze the structural strength of a sample at rest, the $G'(\omega)$ function at the lowest frequencies is usually used. The higher the $G'$ values at low frequencies, the stronger the structure at rest and the more long-term stability can be expected.

From Fig. 12 we obtain the following values for $G'$ and $G''$ at the low frequency $\omega = 0.15$ 1/s:

<table>
<thead>
<tr>
<th>Sample</th>
<th>$G'$ [Pa]</th>
<th>$G''$ [Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>210</td>
<td>30</td>
</tr>
<tr>
<td>Sample 2</td>
<td>105</td>
<td>18</td>
</tr>
<tr>
<td>Sample 3</td>
<td>130</td>
<td>12</td>
</tr>
</tbody>
</table>

For all three samples there is clearly $G' > G''$ over the whole frequency range, even at low frequencies. We can therefore estimate that all three ketchups are stable dispersions which only have a low tendency to separation, even after a relative long period of time.

Fig. 12: Frequency sweeps of the three ketchup samples (all at the constant deformation $\gamma = 0.1$ %). The storage modulus $G'$ and loss modulus $G''$ curves are shown as a function of the angular frequency $\omega$. 

3.3 Structural decomposition and regeneration

3.3.1 Settings

This test characterizes the structure immediately after high shearing or after a vigorous movement of the sample. The time-dependent structural regeneration test gives application relevant information about the sample which goes beyond all the results obtained from the above tests because the pre-handling in this test is a different one as with the flow curves, amplitude and frequency sweeps which are all tests starting from a state of rest. They therefore start from a different pre-condition than is usually the case when we simulate daily processes with foodstuffs.

A combined oscillatory/rotational/oscillatory test with three intervals is carried out.

- 1st interval: Rest before shearing; oscillation in the LVE range with constant deformation $\gamma$ and constant angular frequency $\omega$ (Selected for the tests of Fig. 13 was $\gamma = 1\% = \text{const}$ and $\omega = 10\ 1/\text{s} = \text{const}$. Comment: For Sample 1 and 3, the deformation in the rest interval is a little outside the LVE range - see table in Chapter 3.1.2 - but the test results justify this selection.)
- 2nd interval: Structural decomposition under high shear load; rotational test (here with $\dot{\gamma} = 100\ 1/\text{s}$)
- 3rd interval: Rest for structural regeneration after high shearing; oscillation in the LVE range under the exactly same shear conditions as in the first interval

3.3.2 Test results: Structural decomposition and regeneration

See Fig. 13: In order to evaluate structural regeneration, the $G'(t)$ function in the third interval is compared with the constant value of $G'$ from the first interval; the regeneration is given in %. Full structural regeneration (100 %) occurs fastest with Sample 1; Sample 3 regenerates its structure more slowly, and Sample 2 does not completely regenerate its structure in the observed time span.

<table>
<thead>
<tr>
<th></th>
<th>Sample 1</th>
<th></th>
<th>Sample 2</th>
<th></th>
<th>Sample 3</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>G': start value at rest</td>
<td>420 Pa (100 %)</td>
<td>194 Pa (100 %)</td>
<td>213 Pa (100 %)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G' after t = 30 s</td>
<td>396 Pa (94 %)</td>
<td>138 Pa (71 %)</td>
<td>202 Pa (95 %)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G' after t = 60 s</td>
<td>413 Pa (98 %)</td>
<td>151 Pa (78 %)</td>
<td>209 Pa (97 %)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G' after t = 120 s</td>
<td>in 70 s: 420 (100 %)</td>
<td>160 Pa (82 %)</td>
<td>in 85 s: 213 (100 %)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 13:** Test with 3 intervals to investigate the structural decomposition and regeneration of the three ketchup samples. The first and third interval show the curves of the storage modulus $G'$ and the loss modulus $G''$. In the second interval is presented the time-dependent shear viscosity $\eta$ (from a rotational test).
Note: In this context, terms as “thixotropic behavior” should be used carefully or even avoided because they are not used uniformly and therefore cause confusion in many laboratories. However, to use these terms here: Samples 1 and 3 show 100 % structural regeneration and therefore “thixotropic behavior” in the selected test time (180 s in the third interval). Sample 2 does not completely regenerate its structure in this time, and therefore does not show “thixotropic behavior” correlated to the selected time span.

4 Summary

The structure at rest can be determined using different test methods. In this paper we have covered the following:

- Rotational tests / flow curves: "(apparent) yield point"
  a) as \(\tau\) value just below the lowest shear rate which can be detected by the rheometer, or at another very low shear rate (for test results, see Chapter 2.1.3);
  b) via calculation using approximation functions (regression models).

- Rotational tests / tangent method: yield point
  a) as \(\tau\) value at the upper limit of the elastic range (for test results, see Chapter 2.2.3);
  b) as the tangent crossover point.

- Oscillatory tests (amplitude sweep): yield point
  as \(\tau\) value at the upper limit of the LVE range;
  other parameters which can be analyzed here: structural strength ("rigidity ") as the \(G'\) value (for test results, see Chapter 3.1.2)

- Oscillatory test (frequency sweep): Long-term structural strength at rest as the \(G'\) value at low frequencies (for test results, see Chapter 3.2.2)

- Combined oscillatory / rotational test: time-dependent regeneration of the structural strength as \(G'(t)\) immediately after vigorous shearing (for test results, see Chapter 3.3.2)

The direct comparison of all yield point results obtained from the above test and analysis methods is given in the table below:

<table>
<thead>
<tr>
<th>Method</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Rotation / flow curve (at (\dot{\gamma} = 0.1) 1/s)</td>
<td>11 Pa</td>
<td>12 Pa</td>
<td>7 Pa</td>
</tr>
<tr>
<td>(2) Rotation / tangent method (end of the elastic range)</td>
<td>12 Pa</td>
<td>4 Pa</td>
<td>5 Pa</td>
</tr>
<tr>
<td>(3) Oscillation (AS) / tangent method (end of the LVE range)</td>
<td>10 Pa</td>
<td>3 Pa</td>
<td>5 Pa</td>
</tr>
</tbody>
</table>

The results of the two tangent methods, (2) & (3), are comparable, although one is a rotational test and the other an oscillatory test. The results of the flow curve method (1), however, deviate considerably. This shows that some materials have no longer a stable structure-at-rest when loaded at a shear rate of \(\dot{\gamma} \geq 0.1\) 1/s. Thus in a scientific sense, when using method (1) in this shear rate range the structure-at-rest cannot be characterized properly. Here in this case, the term “apparent yield point” is truly justified.

Conclusion:

We have shown that there are different test methods for determining the structural strength at rest besides the “classic yield point method” from a flow curve using a rotational test. The results from this method are usually insufficient for scientific purposes as the influence of the test conditions (e.g. the limits of the rheometer’s resolution, and dependence on time) is too great. These effects should not be dismissed, even for simple quality control tests.

In order to judge the the long-term stability, the consistency or the character of the structure at rest (as stable viscoelastic gel or unstable viscoelastic liquid), oscillatory tests should be used. The results can be presented in form of the storage modulus \(G'\) (and the loss modulus \(G''\)), or as the limiting value of the viscoelastic deformation range (e.g. given as deformation or as shear stress value).

Literature: Figs. 1 to 3, 6, 8 and 11 are taken from:
Mezger, T.: The Rheology Handbook; for users of rotational and oscillatory rheometers.