

Tips and Tricks from Joe Flow

Sample Preparation: Shaken or Stirred?

Today I would like to discuss the importance and influence of sample preparation in the field of rheometry and give you some tips about how to prepare sensitive samples so that the results are correct and reproducible.

Sample preparation includes removing the sample from the container, shaking or stirring it, filling it into the measuring system, positioning the measuring system as well as the subsequent waiting time or a pre-defined shear before starting the actual measurement.

Depending on the properties of the sample, these preparatory steps have a considerable influence on the results of the rheological measurement. Therefore, sample preparation should always be carried out in the same way every time. This improves the reproducibility of your measuring data, even when many different people operate the rheometer.

Generally, sample preparation has little influence on measurements at shear rates over 10 1/s. However, sample preparation is particularly important when you are measuring at low shear rates or in oscillatory mode, i.e. when investigating the structure at rest to evaluate the stability of the sample. For these reasons, I will discuss each step of the sample preparation process in detail below.

1. Shaking and stirring

Both shaking or stirring a sample puts it under a considerable and undefined shear load. Therefore, they should be avoided if possible. However, samples which separate or sediment must be shaken or stirred in order to perform correct measurements.

Shaking or stirring should be carried out in the same way every time, e.g. using the same tools and for the same amount of time. When measuring PVC plastisols, for example, you should first remove the top layer as this is where the plasticizer often collects or the sample may be dried out on the surface.

2. Application

Each user should use the same tools to take the sample out of the container and apply it. Laboratory spoons or spatulas are the most suitable tools. Depending on the sample properties, you can also pour the sample directly out of the container. To remove the sample from tubes or containers with small openings, cut them open. Pressing sample out of a small opening results in an unwanted shear load which may destroy the samples' structure at rest.

For the same reason, pipettes or syringes are not suitable for sample application. They should only be used with oils, resins or solvents. For all other substances, the high shear load results in reduced measurement values and therefore falsifies the results.

In general, you should always make sure that there are no bubbles in the sample as these have a great influence on the measured value. In flow curves the presence of bubbles may simulate non-Newtonian behavior at low shear and in oscillatory measurements it may simulate elastic properties.

3. Filling volume

The value of rheological variables, e.g. the viscosity, always refers to the size of the measuring system as they depend on the surface size with which the sample comes into contact. Too much or too little sample therefore leads to measurement errors.

If you use cylinder measuring systems, small variations in the filling volume have almost no influence. The filling level is marked on the measuring cups. You should use this as a guideline. The sample must always be well above the upper rim of the inner cylinder.

If you are using cone/plate and parallel plate systems, trimming surplus sample guarantees ideal filling. To do this, apply slightly too much sample to the lower plate and drive towards the measuring position. MCR rheometers automatically stop shortly before the measuring position. Now you need to trim: Remove surplus sample with the straight edge of a spatula. Afterwards, when the rheometer moves to the measuring position a small amount of sample will be pressed out. This procedure has proved to be the best way of filling measuring systems. Trimming guarantees a defined and reliably repeatable amount of sample under the measuring system.

In the software the measuring system can be automatically locked until the measurement starts, therefore preventing it being moved accidentally during trimming (see Fig. 2). This would be an additional and undefined shear load for the sample. If your rheometer does not lock the measuring system automatically you can equip your instrument with this helpful feature by making a software/firmware update.

4. Waiting times, preshearing and other important issues

Even the most careful sample preparation represents a stress for the sample. The sample may only recover from this stress after a certain period of time. If you notice at the start of the measurement that the measurement values at low shear rates or in oscillation increase, it may be that the sample structure needs to regenerate after the positioning of the measuring system. Another reason for an increase in the measured values could be that the sample surface has dried out. Curing reactions are special cases. With curing reactions the measurements are started immediately, without waiting time, so that the course of the reaction can be observed from the beginning.

If the substance you want to measure requires time to recover after application, set a waiting time in the Start dialog in the software. You do not need a stopwatch and every measurement begins after the same period of waiting time. You can determine the length of the waiting time in a pretest, as shown in Fig. 1. You record the behavior of the sample over a long period of time under constant measurement conditions (frequency and deformation in the linear-viscoelastic range for oscillatory tests or small shear rates of e.g. 0.1 1/s for rotational tests). Afterwards you can see how long it takes before the changes become small enough to start the "real" measurement.

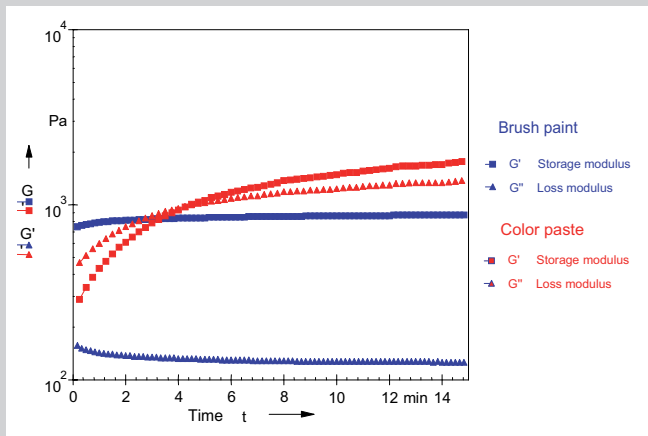


Fig. 1: Structural regeneration after the application of paint

According to the measurements in Fig. 1 the paint needs approx. 1 minute and the color paste needs at least 15 minutes waiting time. In this waiting time the temperature of the sample is also controlled (see Tips and Tricks from Joe Flow: Temperature Control).

If the sample is very sensitive you can drive to the measuring position more slowly. The speed can be set in the control panel of the software (Fig. 2).

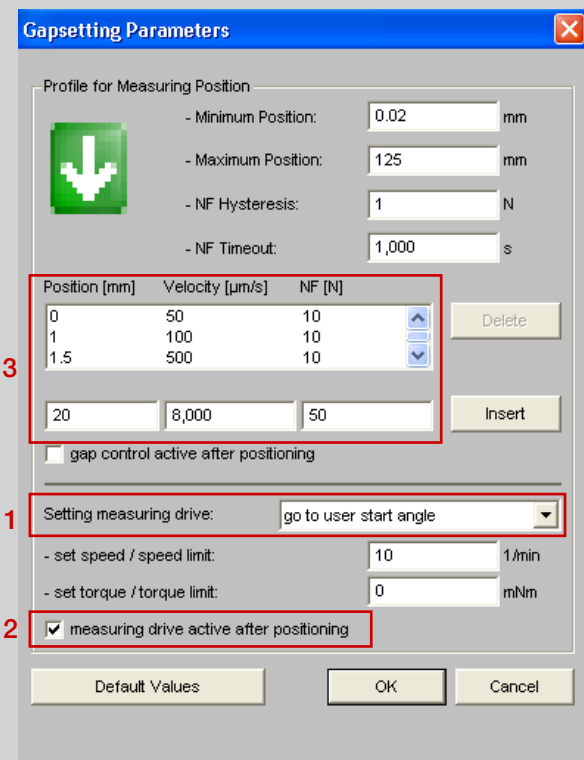


Fig. 2: Gap-setting parameters and moving profile for the measuring position

- 1) When the measuring system moves to the measuring position it is locked.
- 2) After reaching the trim position the user is prompted to trim the sample. The measuring system is still locked until the test is started.
- 3) The velocity of movement can be set individually.

It is important to prevent the sample surface from drying, otherwise the measured values will be too high. If the sample and working environment allow it, you can apply a very low-viscous oil to the outer edge of the sample before an oscillatory measurement is started. Another option is the use of the "Evaporation Blocker", which seals the sample area from the environment. The sample area can also be saturated with a suitable solvent.

Fig. 3 shows two measurements which were carried out with and without an Evaporation Blocker. Without an Evaporation Blocker, the drying of the sample causes an increase in the moduli which is shown in the results. With the Evaporation Blocker the moduli remain at a constant level.

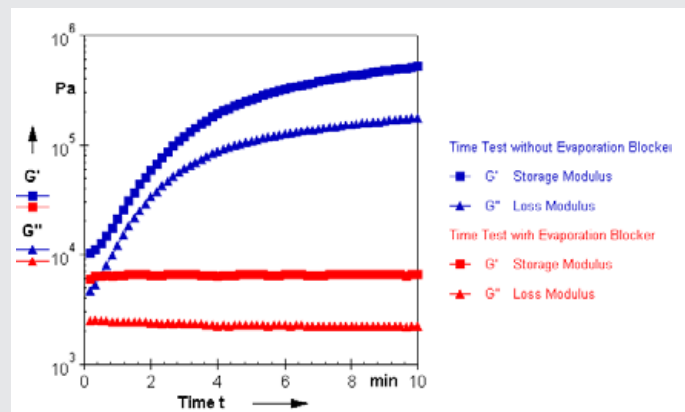


Fig. 3: Time test in oscillation at 35 °C with and without an Evaporation Blocker

Liquid samples which dry out very quickly should be measured in a cylinder measuring system because with these systems the influence of the dried surface is extremely small.

Substances which react with oxygen in air should be measured in an inert atmosphere saturated with nitrogen.

Instruments for:

Density & concentration measurement
Rheometry & viscometry
Chemical and analytical techniques

Colloid science
X-ray structure analysis
CO₂ measurement
High-precision temperature measurement