Water present on the surface of the crystals evaporates more rapidly than water that has to reach the surface through diffusion. The rate of loss of weight therefore momentarily increases.

Conclusions
DSC microscopy allows images of a sample to be simultaneously recorded by a camera while the sample is measured in the DSC 1. Visual changes can be documented and correlated with effects on the DSC curve. DSC microscopy can detect:
- color changes as a result of chemical reactions (decomposition) or polymorphism, and
- changes in the "geometry" of samples, for example as a result of melting or flowing, shrinkage or expansion, movement of the sample during glass transitions or solid-solid transitions, or the formation of cracks.

The visual information from the microscope often greatly facilitates the interpretation of physical-chemical effects observed in DSC curves. DSC microscopy is therefore a very useful accessory for studying materials by DSC.

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Sample preparation for DMA shear measurements

Jing Ni

Careful sample preparation is crucial for good quality DMA shear measurements. The most important influence factors are discussed with the aid of practical examples.

Introduction
In the DMA shear mode, two identical samples are clamped between the three clamping plates of the shear sample holder. The two outer plates are fixed in the clamping assembly while the oscillating force acts on the center plate.

The shear mode is widely used for materials with very different physical properties and geometries such as soft elastomers, hard composites, viscous liquids, powders, and plastic films.

The following section presents some general tips on sample preparation concerning
- the geometry of samples
- tools for preparing samples
- clamping and predeformation
- installation in the clamping assembly
- measurements below room temperature.

General tips on sample preparation

Geometry of samples
- Optimum shear samples must have plane parallel surfaces.
- The geometry factor should be between 20 and 50 m^{-1}.
- The diameter should be at least three times greater than the thickness in order to make sure that the sample undergoes shear and is not bent.
- The stiffness of the sample should be at least five times smaller than that of the measuring device. Otherwise, the resulting values for the shear modulus are too low.

Tools for preparing samples
Use the right tools in order to obtain the desired circular disk or rectangular bar from the material you want to measure:
- sample punch, carpet knife or scissors for soft materials such as rubber sheets or plastic films;
- diamond saw for hard samples such as fiber composites;
- small hydraulic press (KBr press) to press disks from powders.

Clamping and predeformation
When you clamp the sample in the shear sample holder, remember that clamping also predeforms the sample. Proper clamping ensures that the sample does not slip. Samples are often too strongly predeformed.

We recommend finger-tight clamping. In particular, with small, hard samples, the left shear plate with the thermocouple could be damaged if a screwdriver is used for clamping.

Installation in the clamping assembly

When the shear sample holder is installed in the clamping assembly, first tighten the middle screw (5) using a torque of 0.5 to 0.8 Nm and then tighten the remaining four screws (1 to 4) diagonally using the same torque (Figure 1).

Figure 1.
Installing the shear sample holder in the clamping assembly.

Measurements below room temperature

If the measurement begins below room temperature, the sample usually shrinks slightly on cooling. The contact between the sample and the shear plates is then no longer optimal. Retighten the sample about 10 K above the start temperature.

Difficult samples such as thin films and very stiff materials require further measures to obtain reliable and trustworthy results. The following sections present a number of tips for handling these types of sample.

Very stiff materials

Hard and stiff samples are best measured in tension or in 3-point bending. Sometimes the shear mode is used, either because a customer requests this or because the amount of material available is too small for the tension sample holder or the 3-point bending accessory.

One problem encountered with hard samples is that their surfaces are often not ideally plane-parallel. The sample is then only in partial contact with the clamping plates and the shear force acts on just part of the surface area (Figure 2). The geometry factor is then much smaller than the calculated value and the shear modulus is also too small.

With samples like this, the area of contact is not constant. This leads to poor reproducibility of the shear modulus, particularly in the glassy state.

To ensure that the sample used for shear measurement makes contact over its entire surface area, we recommend that you clamp the sample at a temperature above its glass transition temperature. It generally shrinks slightly on cooling and contact between the sample and the shear plates is no longer so good. Retighten at the start temperature.

Figure 3 shows the measurement of a cured epoxy resin and the improvement achieved by clamping the sample above the glass transition point, T_g, as described above.

At 25 °C, the shear modulus increased to about 1.2 GPa (blue curve), which agrees well with the Young's modulus value of 3.4 GPa determined in tension. Clamping at room temperature resulted in a value for the glassy state that was too low (0.55 GPa, red) because the surfaces of the sample were not quite plane-parallel.

Soft elastomer samples

The reproducibility and accuracy of the shear modulus measurement of an elastomer in the rubbery state are also influenced by sample preparation. The following sections cover the most important influence factors [1]:

Geometry

The shear modulus is a material property and should be independent of the size of the test specimen measured. In certain cases, this does not always seem to be true. This is illustrated in Table 1, in which the measured values of the shear modulus are shown for three test specimens (disks). The material was the same but the diameters were different. Each test specimen was measured ten times without removing the sample holder and test specimen (repeatability measurements).

The modulus increases with increasing diameter of the test specimen. The reason for this can be attributed to so-called boundary effects. The disks were prepared using a punch and were not perfect cylinders – their circumference was slightly narrower in the middle. The effective diameter was therefore slightly smaller than the diameter of the punch.

This error becomes less important with increasing diameter. Punching out soft samples is actually not the ideal way to prepare such test specimens. In practice though, what is the alternative? It is not so easy to cut out a rectangular sample with exactly vertical sides from a rubber sheet using a sharp knife either.

Predeformation

Predeformation of soft samples through clamping reduces the thickness of the test specimen. Assuming that the total volume of the specimen does not change, the cross-sectional area becomes correspondingly greater. These two effects lead to an increase in sample stiffness.

If the change in geometry is taken into account in the calculation of the geometry factor, the measured modulus value should not change.
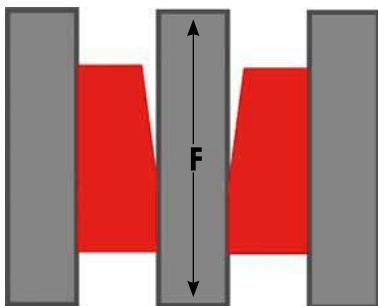
Figure 2.
The sample is not suitable for shear measurement. The surfaces are not plane-parallel so the contact area is much smaller than the area of the sample.

Table 1.
Shear modulus measurements of disks of different diameter.

Diameter in mm	Mean value of the storage modulus in kPa	Standard deviation in kPa
4	448.5	6.7
5	465.9	3.5
6	500.9	4.9

In fact, however, with soft elastomers a decrease in the modulus is observed when predeformation is increased (typically about 1% per percent predeformation). The reason for this is that the test specimen bellies out due to predeformation, which makes an accurate determination of the geometry factor impossible. Furthermore, the test specimen may already be stressed by the predeformation to such an extent that the measurement is no longer within the linear range of the material. This also leads to a smaller modulus value.

It follows that predeformation should be as small as possible (< 5%). In practice, with very soft samples, it is however difficult to reproducibly set low predeformation.

Creep

Weakly vulcanized elastomers exhibit a more or less pronounced creep (plastic deformation). Besides the degree of vulcanization, the filler content also influences the creep behavior.

As shown in Figure 4, the measured modulus increases systematically with time while the standard deviation decreases. This can be explained by assuming that the test specimen adapts to the clamping force, which takes time. In this example, the modulus increases by about 0.3%/min during the first 30 min.

This effect is only observed if the measurement is started immediately after sample preparation, and ideally isothermally at room temperature with the furnace open. If a freshly clamped test specimen is left for an hour, it has time to adapt to the shear plates through creep and the modulus value obtained is constant.

Repetition of a measurement with re-clamping of the sample

Removal and re-clamping of the same test specimen in a shear sample holder with a predeformation of say 10% leads to a spread of the values obtained for the storage modulus of about 5%. This spread is mainly determined by the reproducibility of the predeformation.
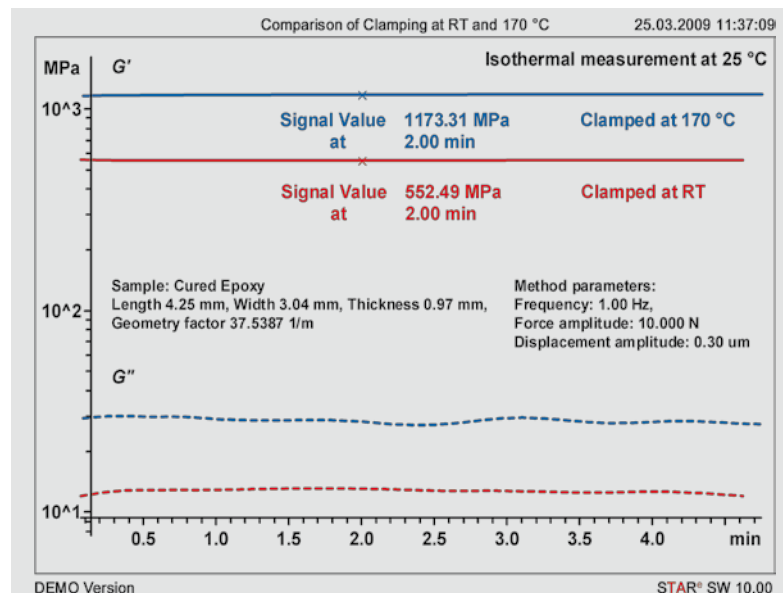
Figure 3:
Determination of the shear modulus of a cured epoxy resin at 25 °C. Above, red: the incorrect shear modulus because the sample surfaces were not plane-parallel. Above, blue: the sample was clamped above the glass transition temperature at 170 °C; the modulus value is now correct due to the improved contact between the sample and the shear plates.

The uncertainty of the storage modulus measurement of a 10% predeformed elastomer sample of 5-mm diameter at room temperature is mainly due to inaccuracies in the predeformation and sample geometry. The combined uncertainty is about 12%.

Anisotropic materials

Anisotropic materials exhibit properties that vary with the spatial direction in which they are measured. Examples of such materials are fiber-reinforced plastics, such as fabric-reinforced laminates or thermoplastics filled with relatively long fibers. Such composites consist of fibers (e.g. glass or carbon fibers) with a very high modulus and a much softer matrix.

Other composites consist of metal fibers or foils and polymers. DMA measurements of anisotropic samples yield different results depending on the direction in which the stress is applied: If the shear force acts parallel to the fibers in the composite, the softer matrix dominates because in this case the compliances normalized for thickness are additive (Figure 5 above, left) [2].
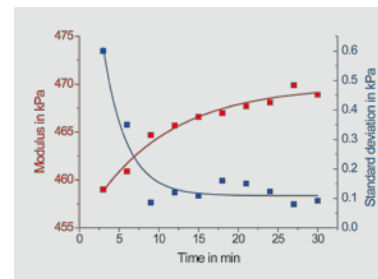
Figure 4.
Shear modulus and standard deviation of a weakly vulcanized rubber sample at room temperature. The modulus of the freshly clamped test specimen shows a significant increase during the first 30 min.

The soft matrix dominates the measurement.
d_1 and d_2 are the individual thicknesses of the two components.
The stiff reinforcement material dominates the measurement.
A_1 and A_2 are the individual areas of the two components.

$$J = \frac{J_1 d_1 + J_2 d_2}{d}$$

$$E = \frac{E_1 A_1 + E_2 A_2}{A}$$

Matrix material
Fibers

Stiff material dominates
Soft material dominates

$$G = \frac{G_1 A_1 + G_2 A_2}{A}$$
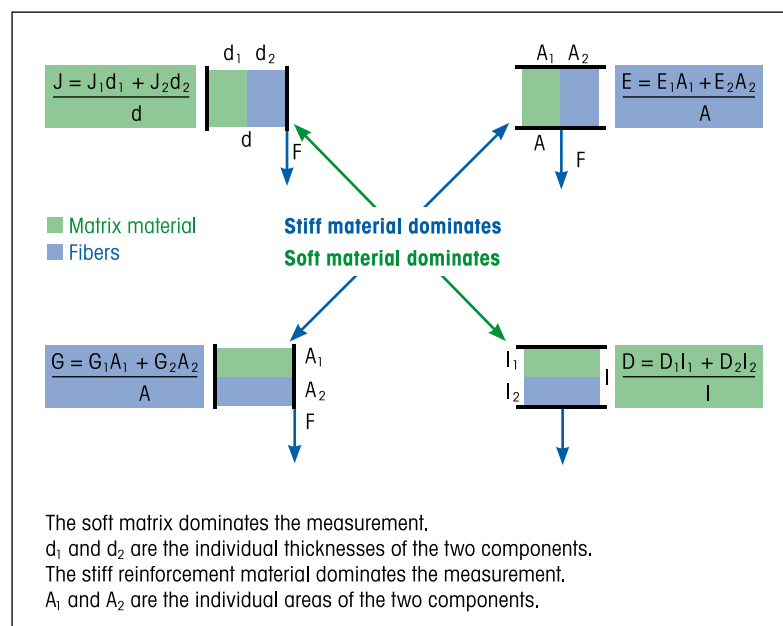
$$D = \frac{D_1 l_1 + D_2 l_2}{l}$$

Figure 5.
Schematic diagram of the shear and tension measurement (tension is for comparison) of a two-layer laminate in both directions. The green area corresponds to the matrix, the blue area to the reinforcement material.

The situation is quite different when the shear force acts at right angles to the direction of reinforcement. In this case, the moduli normalized for area are additive and the stiffer component determines the total modulus (Figure 5 below, left) [2].

The orientation is chosen depending on the information required. If one is interested in the glass transition of the matrix resin, the measurement is performed parallel to the direction of the fibers. In this case, the compliance yields more detailed results (Figure 6).

Figure 6 shows the measurement of a laminate consisting of a 0.4-mm thick aluminum foil coated with two layers of different elastomers. The shear measure-ment was performed at 10 Hz in a direction parallel to the layers. The modulus curves and the loss factor show just one glass transition at about −20 °C. The glass transition of the other elastomer is only visible as a weak shoulder that is easily overlooked on the tan delta curve at about 20 °C. Due to the additivity of compliance contributions, the two transitions are easier to see in the compliance curve, (J'').

Thin plastic films

Thin plastic films are often measured in tension. Under certain conditions, reli-able results are also obtained from shear experiments. As in any DMA measure-ment, the stiffness of the sample must be at least five times smaller than that of the measuring device. Otherwise, the measured value of the shear modulus is too small. The clamping assembly with the shear sample holder has a typical stiffness of $1.38 \cdot 10^8$ N/m. This means that the sample stiffness must not be greater than $3 \cdot 10^7$ N/m.

Example: What is the maximum area A of a sample disk made from a plastic film of thickness d = 140 µm and an assumed modulus M´ = 1 GPa?

$$A = \frac{1}{2}\,d = \frac{3 \cdot 10^7\ \text{N/m}}{\text{M}´} = 2.1\ \text{mm}^2$$

Substituting in the equation gives an area of 2.1 mm², which corresponds to a diameter of 1.7 mm. Such small disks are difficult to clamp because of the pos-sibility that adjacent shear plates tilt and touch each other.

The sample stiffness can not therefore be reduced by decreasing the diameter of the disk. An alternative is to increase the sample thickness by stacking several disks on top of one another. To prevent the sample disks from slipping and to enable reproducible sample preparation, we recommend that you separate the in-dividual sample layers using aluminum disks.

If the sample stiffness is too high, large errors in the modulus occur (Figure 7, blue curve). By reducing the sample stiff-ness, a realistic modulus value of GPa in the glassy state is obtained (red curve). Both loss factor curves show a glass tran-sition at about 5 °C and the beginning of melting at about 38 °C.

Viscous liquids and pastes

Liquids and pastes can be measured in the specially designed shear sample hold-er for liquids (Figure 8). The distance between the shear plates is set using a thickness gauge before filling the sample into the two spaces at room temperature.

This is done using a spatula, a pipette, or a syringe depending on the exact nature of the sample. For low viscosity liquids, it is better to use a small sample thick-ness. After installing the shear sample

Figure 6.
DMA measurement of an aluminum foil with two different elastomer layers. The shear force acts in the direction parallel to the lay-ers. The compliance curve (J˝) shows more detail.
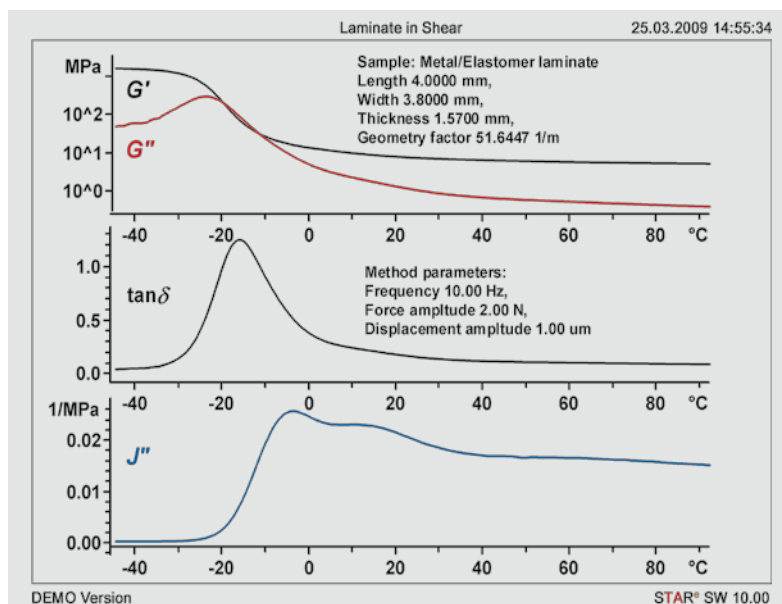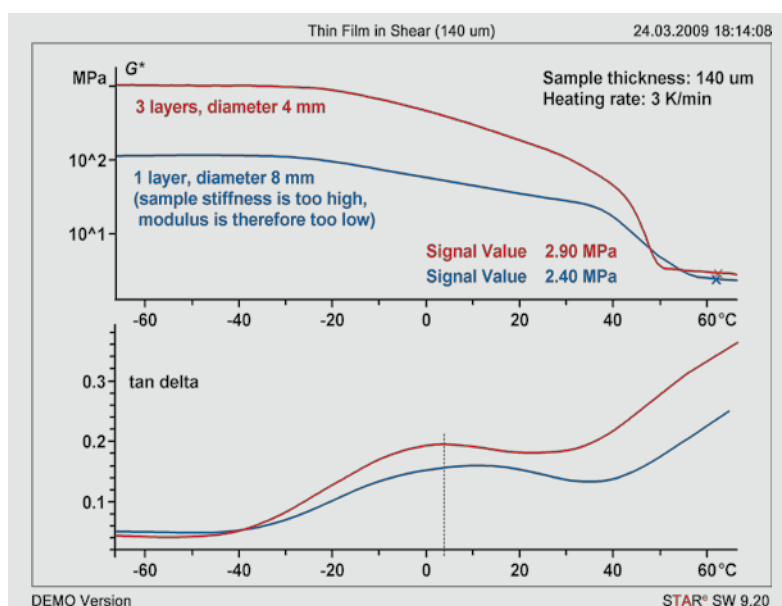

Figure 7.
DMA measurements of a 140-µm thick plastic film.
Blue: one disk of 8 mm diameter yields a modulus that is too low be-cause the sample stiffness is too high.
Red: a sandwich of three disks of 4-mm diameter gives cor-rect values.

holder in the clamping assembly, the two guide rods ①, and then the four distance screws ② are removed. The smallest viscosity that can be measured is about 0.03 Pa· s.

The viscosity of the sample, η′, can be calculated from the shear loss modulus, G″, and the frequency, f, according to the following equation [3]:

$$\eta' = \frac{G''}{\omega} d = \frac{G''}{2\pi f}$$

In Figure 9, the upper curves show the moduli of an epoxy resin-hardener mixture as a function of the sample temperature. The lower curve shows the viscosity calculated from the loss modulus. The sample is initially at −50 °C in the glassy state. It becomes liquid above the glass transition temperature of −15 °C.

With increasing temperature, the viscosity sinks to a minimum of about 0.02 Pa·s at 110 °C. The viscosity then increases again due to the continuing curing reaction. The gel point temperature is about 150 °C. Toward the end of the curing reaction, the storage modulus reaches a value of 10 MPa, which shows that the final product is rubbery above its glass temperature.

Summary

Many materials with quite different physical properties and geometries can be easily measured in the shear mode. The advantages of the shear measurement are:

- no offset force is required as is the case for bending or tension,
- the sample temperature is accurately measured,
- a very large stiffness range can be covered in one measurement (up to 8 decades).

Careful sample preparation is crucial for obtaining reliable and reproducible results. The stiffness of the test specimen measured must be at least five times smaller than the stiffness of the sample

clamping assembly, that is, not greater than $3 \cdot 10^7$ N/m.

With thin films, this can often be achieved by stacking several layers of the film separated by aluminum disks to form a sandwich. This increases the effective thickness of the film.
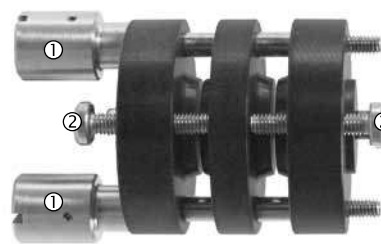

Figure 8.
The shear sample holder for liquids with the two guide rods (1) and the four distance screws (2). The two spaces are ready to be filled.
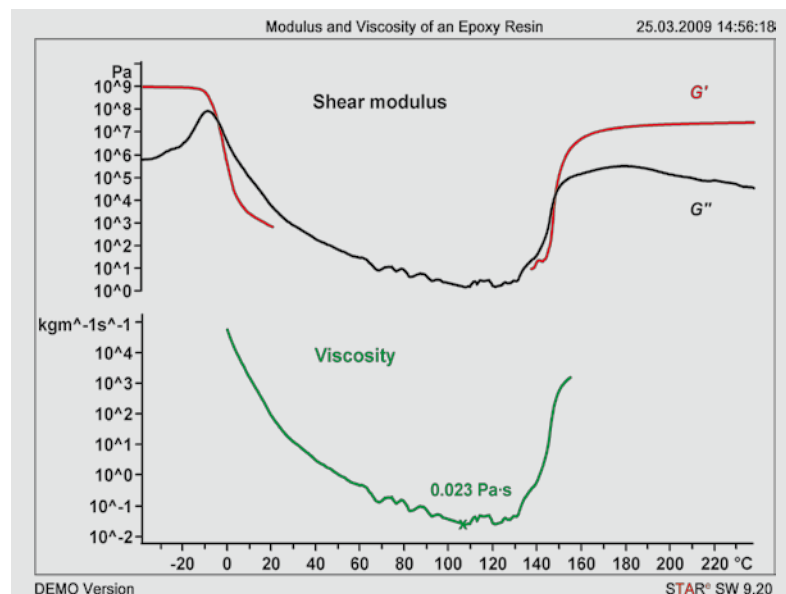

Figure 9.
DMA heating curves of an epoxy resin-hardener mixture in the shear sample holder for liquids.

The most important point for reliable shear measurements is to make sure that the entire area of the test specimen is in good contact with the shear plates. If the starting temperature of the measurement is significantly lower than the clamping temperature, the test specimen may possibly have to be re-clamped. In any case, at the beginning of the measurement (i.e. at the start temperature), the modulus should have a plausible value.

Elastomers are materials that are typically measured in shear. The uncertainty of the modulus value in the rubbery plateau of elastomers is determined by the reproducibility of the predeformation and the sample geometry. It is about 12% of the modulus value.

With anisotropic materials such as laminates, the orientation of the sample is very important. If the sample is installed so that the layers are parallel to the applied shear force, the soft components determine the mechanical behavior. In this case, the

compliance gives the clearest information about the sample. In contrast, if the layers are at right angles to the applied shear force, the hard components determine the behavior of the sample.

Liquids and pastes can be measured with the sample holder for liquids. The viscosity can also be calculated from the loss modulus in such experiments.

It is also possible to measure powders in the shear mode. To do this, two disks are pressed from the powder (typical dimensions: diameter 4 mm, thickness 1 mm) and then clamped between the shear plates.

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[2] J. Schawe, UserCom 26, 1–4.
[3] R. Riesen, Thermosets 28–30, Thermal Analysis Collected Applications, METTLER TOLEDO.