

## Rheometry of complex fluids

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### Abstract

The difficulties involved in measuring rheological characteristics of complex fluids are discussed. Possible measurement errors, related to the complex nature of the sample, are reviewed. They are explained in terms of the various physical and chemical mechanisms that can cause them. This leads to possible strategies and techniques for avoiding measurement errors and for obtaining useful structural information from rheological experiments on complex materials. Finally, future evolutions in rheometry are discussed.

### 1. Introduction

Unlike what is customary with many other types of measurements, it is impossible in rheometry to establish general procedures for performing measurements and analyzing data that will always generate real material characteristics of the sample under consideration. In some cases it is very difficult to obtain reliable and physically meaningful measurement results. Furthermore, no suitable rheological models are available for several classes of materials, hence no model parameters can be derived from the measurements. Examples of such rheologically complex systems abound. Whereas ordinary polymer melts and solutions can be handled relatively well, this is not the case for more complex polymeric systems, including phase-changing solutions, blends, block copolymers and liquid crystalline polymers. Besides polymers, difficulties often arise in two-phase systems such as suspensions and emulsions and systems with complex phase behaviour, e.g. surfactant solutions. A large percentage of industrial and even naturally occurring fluids belongs to these categories: various types of structured polymers, food products, pharmaceuticals, cosmetics, industrial pastes and slurries, sealants, propellants, naturally occurring slurries, etc. The rheometry of such materials is discussed here.

### 2. Measurement problems

First the phenomena are discussed that can be observed during rheological measurements and that indicate deviations from the flow behaviour that is assumed in the data analysis. They are grouped, somewhat arbitrarily, in two major classes: those related to geometry effects and those related to time effects. These classes are not mutually exclusive. The underlying physical and chemical *mechan-*

*isms* are dealt with in section 3.

#### 2.1. Geometry effects

A rheological characteristic, derived from a measurement, is a real bulk property of the sample when its value describes flow under different conditions and in different geometries. Conversely, it should also be possible to derive the same material properties from flows in different geometries, at least when the type of flow (e.g. simple shear flow, uniaxial extensional flow) remains the same. When different geometries produce different results, even after correcting for end effects and shear rate distributions (see e.g. Macosko, 1994), this suggests errors in the measurement or in the data analysis. Liquid crystals are in a certain sense an exception to this rule as their flow behaviour depends intrinsically on an external length scale. After taking this into account in the experiments and in the data analysis, it should be possible, at least in principle, to

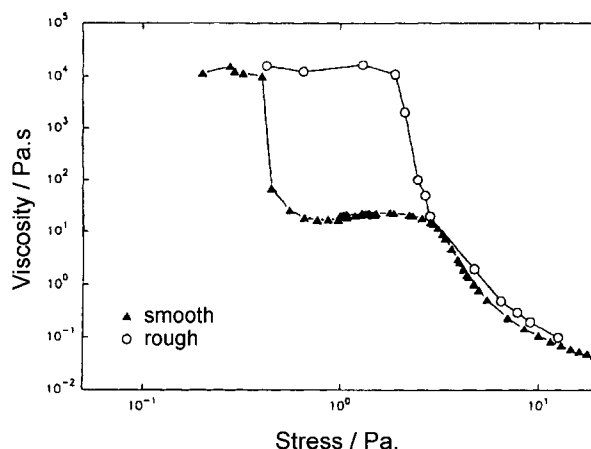


Fig. 1. Difference between measurements on a non-aqueous polymer dispersion with smooth (filled symbols) and rough (closed symbols) inner cylinder in Couette geometry (from Buscall *et al.* (1993), with permission).

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derive fundamental characteristics for this class of materials (Fisher and Frederickson, 1969).

The most common geometry effect is observed when the dimensions of the gap are varied. When data, obtained with different gap sizes, do not superimpose this indicates that the assumed kinematics are not satisfied. The cause is often related to abnormal large velocity changes near the wall. Such wall slip is well known and quite well studied, at least for common classes of fluids as polymers (Macosko, 1994), although the phenomenon is not totally understood. Slip velocity is normally controlled by the wall stress. It might also depend on the wall material and on pressure, thus complicating a comparison between measurement geometries (Hatzikiriakos and Dealy, 1992).

The occurrence of wall slip is not limited to polymers. Suspensions often display the same problem. This is illustrated in figure 1 (Buscall *et al.*, 1993). In this particular case different gap sizes in a Couette geometry, using smooth cylinders, resulted in an intermediate plateau in viscosity, the level of which depended on the annular gap size. With a roughened inner cylinder this plateau disappeared, producing a drastically different viscosity curve. The effect of wall roughness suggests that wall slip is the cause of the observed deviations. Wall slip can also be encountered in concentrated suspensions at high shear rates, where shear thickening occurs (Laun *et al.*, 1991).

Gap size effects are not the only possible type of geometry effects. Often differences can be noticed between results obtained with a capillary and those from a cone and plate, even between capillaries and slit dies (Laun *et al.*, 1991). A simple case, comparing results from a cone and plate and a Couette geometry, is shown in Fig. 2 (Raynaud, 1997). It will be further discussed below.

2.2. Time effects

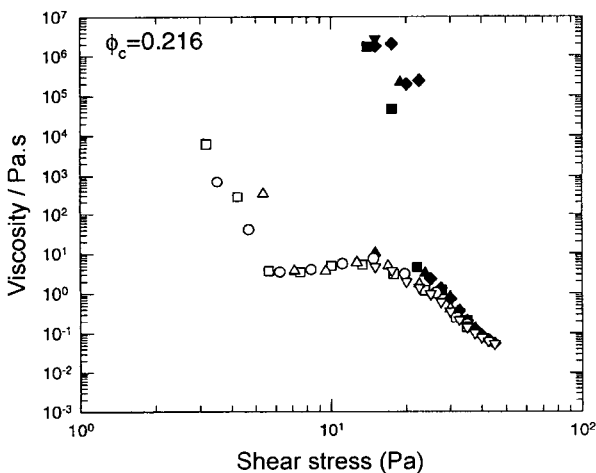


Fig. 2. Effect of geometry on the flow curve of a TiO<sub>2</sub> suspension (filled symbols: Couette; open symbols: cone and plate) (Raynaud, 1997).

Time effects can interfere in various ways with rheological experiments, whether they are intrinsically related to the rheological nature of the sample or caused by some interference of the measurement procedure. Sometimes the changes in time are irreversible. Irreversible changes that occur throughout the sample, e.g. a polymerization reaction, can be the object of the study. Such systems can in principle be described by combining expressions for the time evolution with constitutive equations. On the other hand accidental irreversible changes, like evaporation of volatile components, will interfere with the measurement. To a certain extent they can be counteracted by adapting the measurement procedure, but they can also seriously limit the measurement possibilities.

As long as the changes are homogeneous throughout the sample, the measurements reflect at least the correct instantaneous properties of the evolving system whether the changes are wanted or not. Non-homogeneous changes always affect the measurements. They can be responsible for additional geometry effects. Their appearance is not limited to irreversible time phenomena such as evaporation. Slow reversible time effects often reflect large non-homogeneous structural changes in the material, either intrinsic ones or instrumental artefacts, that should be evaluated carefully to avoid major errors (Laun *et al.*, 1991).

Slow changes always complicate the measurements. Even when they are homogeneous and reversible they make it very difficult to achieve real steady state conditions. This might result in hysteresis phenomena or even in apparently irreversible behaviour. The possible effect of slow changes is demonstrated in Fig. 3 (Ourieva, 1999). The sample is a weakly flocculated suspension of sterically stabilized PMMA particles. The lower curve represents the viscosities measured after shearing the sample at 100 Pa and then

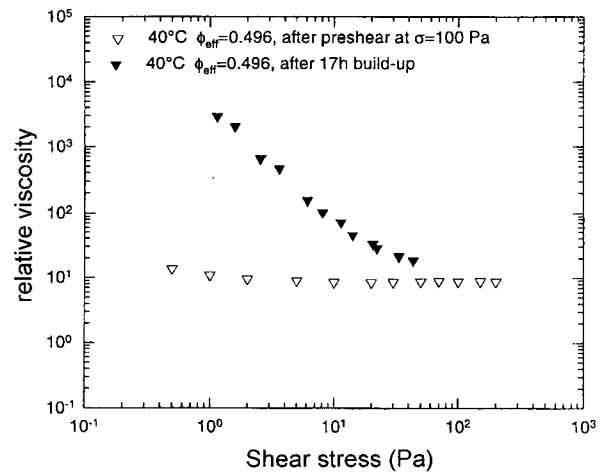


Fig. 3. Effect of shear history on the viscosity curve for a suspensions of PMMA particles: immediately after shearing (open symbols), after 17 hrs rest (closed symbols) (Ourieva, 1999).

decreasing the stress stepwise, waiting each time 1000 s before taking a reading. The upper curve has been obtained after a rest period of 17 hours, after which the shear stress was increased stepwise, recording each time the apparent steady state viscosity. At high shear stresses the results of the two procedures approach each other, but at low stress levels the differences reach several orders of magnitude.

### 3. Underlying mechanisms

Here, the physical and chemical mechanisms are reviewed that cause real or apparent complex rheological behaviour. Flow instabilities, physical and chemical ageing of the sample and flow-induced changes in structure are considered.

#### 3.1. Intrinsic deviations of the flow pattern

Even without any structural changes or any wall slip, the intrinsic rheological nature of the sample can cause deviations from the assumed flow pattern. Consequently, errors will be made while calculating the rheological properties. These intrinsic changes in flow pattern are caused by secondary flows and other flow instabilities (Macosko, 1994). Secondary flows can even occur with simple fluids: e.g. Taylor vortices in Couette geometries. Viscoelasticity often accelerates the onset of instabilities or causes additional types of instabilities. They are quite well documented for polymer melts, although not completely understood. A case in point is shear fracture or edge failure, a distortion of the surface of the sample in rotational rheometers. It causes the sample to creep out of the gap in cone and plate or parallel plate geometries, resulting in a reduction of the effective cross section of the fluid (Hutton, 1969).

Slip layers constitute another type of instability which is often encountered with highly shear thinning materials at relatively low shear rates. Under these conditions it becomes increasingly difficult to ensure a well defined velocity profile. This also holds for geometries in which the shear rate is normally assumed to be constant, such as coaxial cylinders or cone and plate (Cheng, 1966; Ladyzhinsky and Urieu, 1996). In a plastic-like material there is no mechanism to distribute the velocity difference evenly over the gap. Hence, slip layers or shear bands can develop at the wall or in the bulk. As a consequence, the shear rate in the sample is not homogeneous or well defined anymore. This situation arises in power law fluids with a very small power law index, including materials with a yield stress when the applied stress is close to that value. In a Couette geometry the yielding will start near the inner cylinder where the stresses are somewhat larger. Therefore, slip will also be initiated at this cylinder. This explains the results shown in Fig. 1. A somewhat similar situation can arise in systems without a one-to-one relation between shear stress and shear rate (Coussot *et al.*, 1993). Obviously this would give rise to hysteresis phenomena when increasing and

decreasing shear stress or shear rate. Instabilities and secondary flows require time to develop, they also will depend on the measurement geometry.

Finally it should be mentioned that the intrinsic deviations in the velocity profile can occur in coarse two-phase systems such as suspensions, even without instabilities and secondary flows in two-phase systems. When there are substantial velocity changes over length scales comparable with the size of the particles, the assumption of an undisturbed velocity profile is invalidated. Near the wall this can give rise to apparent wall slip, because the concentration of particles is bound to be smaller in a region having a thickness of the particle radius. The lower concentration will cause a lower viscosity and therefore higher velocity gradients near the wall. As a rule of thumb these effects become substantial with objects that approach approximately 1/10 of the gap size.

#### 3.2. Irreversible time effects

Not all samples that are being measured are stable. Rheometry can actually be used to follow the time evolution in materials. Sometimes the sample represents a material that is changing in an industrial process; the modeling of such a process can require that the rheological properties be known at each instant. In other cases the change in time is a side effect of the measurement which one wants to eliminate, or at least reduce as much as possible. The mechanisms discussed here do not require flow. They can, however, be accelerated by shear. Intrinsic shear effects are discussed in 3.3.

A distinction can be made between physical and chemical changes. Various chemical reactions can occur during measurements, especially in polymers. Polymerization has already been mentioned. While measuring polymers, mechanical, thermal and other types of degradation can change the molecular structure, thereby altering the rheological properties. Some reactions can involve other components, such as water in polycondensation reactions. Chemical modifications within the polymer are illustrated by transesterification reactions. Of course many other types of chemical reactions are possible. If not intentional, precautions should be taken to avoid such reactions or limit their impact on the measurements (e.g. by drying samples or controlling the measurement atmosphere).

Physical changes are often reversible but they can occasionally be irreversible or quasi-irreversible as well. An irreversible, physical change can be caused by components that diffuse in or out of the sample by absorption or evaporation respectively. In multiphase systems changes in the phase behaviour can alter the composition and the amount of each phase. Also the size of the phases or the structural units can be affected: e.g. in colloidal unstable systems clusters of particles can develop and grow in size because of aggregation. In case of incompletely dispersed

suspensions the reverse can happen when the degree of dispersion slowly increases in time. In emulsions coarsening of the droplet structure can occur, e.g. because of Ostwald ripening. Phases can even emerge or disappear, e.g. by precipitation (crystallization) or dissolution of a phase. Some of these changes are accelerated by shear. One that might be reduced by flow is the development of concentration gradients because of density differences between phases. The result of e.g. sedimentation will depend on the geometry used. This is illustrated in Fig. 2. The sample used there contained  $\text{TiO}_2$  particles, which are not neutrally buoyant in water. Some degree of sedimentation occurred during the measurements. The effect is more pronounced in cone and plate geometry, where a layer depleted of particles develops near the upper tool. In a Couette geometry sedimentation has to be much more pronounced before it affects the measurements substantially.

Irreversible changes during the measurements are not necessarily caused by the sample itself. Stability of the instrument becomes an issue in experiments of long duration, as is often necessary with complex, structured samples. Over extended periods of time the gap setting in parallel plate or in cone and plate geometry as well as the zero setting of the stresses can drift. This has to be taken into account in some measurements, such as very accurate, slow relaxation experiments (Modenaers and Mewis, 1990). Especially the normal stresses cause difficulties in this respect.

### 3.3. Shear rate effects

A distinction should be made between changes that are controlled by the shearing motion itself and those that are induced by the presence of gradients in shear rate. For the time being only flows with essentially a constant shear rate are considered. In that case the flow can cause the same structural changes throughout the sample, preserving a homogeneous structure. This is, however, not necessarily so and the consequences of heterogeneous structures have to be considered. It should also be mentioned that shear-induced changes in microstructure also evolve in time. Applying a constant shear stress or shear rate therefore produces different shear histories. This will result in different rheological transients and even cause different intermediate structures, a phenomenon which has been called structural hysteresis (Mewis *et al.*, 1975). Finally, the changes caused by the flow can be reversible or irreversible, a distinction which will affect the measurement strategy.

#### 3.3.1. Reversible, homogeneous changes in structure

Many materials display an intrinsic time-dependent behaviour. In principle all non-Newtonian behaviour can be attributed to some reversible, flow-induced, microstructural changes. It could indeed be argued that these changes do

not develop instantaneously and hence are associated with an intrinsic time scale. In polymeric systems stretching, orientation and disentanglement of the macromolecules is responsible for the classical viscoelastic response. This lowest level of complexity is considered to be part of the basic rheological behaviour of such systems. It is covered by the molecular theories and is not further discussed here. There is no clear transition with the more complex, structured materials. Examples of a somewhat more complex systems are simple colloidal suspensions, where the changes in the orientation and/or relative position of particles with shear rate cause non-Newtonian behaviour and, to a certain extent, also time effects. Also in the case of simple colloids some microrheological theories are available or are emerging.

The situation becomes definitely more complex, and so do the measurements, when structural features at somewhat larger length scales are involved. Sometimes structural units, such as molecular aggregates (with associating polymers or in micellar systems), flocs or aggregates of particles (in colloidal suspensions), droplets or bubbles (in emulsions, polymer blends or foams), domains (in block copolymers and liquid crystalline polymers) appear, disappear or change because of the flow. Such changes can cause rather complex changes in rheological behaviour. As long as they are reversible and a function of the shear history of the physical points, they could in principle be incorporated in rheological models. This has been done for the reversible intermolecular rearrangements induced by flow in worm-like micelles (Cates, 1987) and also for some associative polymers (Semenov *et al.*, 1995).

The reversible changes in structure caused by flow can even be more substantial. Consider for instance the case of real, flow-induced, phase transitions. Examples can be found in flow-induced phase separation or mixing in polymer solutions, order-disorder transitions in colloidal suspensions, different phase transitions in micellar surfactant solutions, phase inversion in liquid-liquid systems. The rheological effects of these structural changes are quite variable. Flow can induce growth or decay of structures. As a consequence viscosities can increase or decrease as a function of time or shear rate. Often the effect of the shear history deviates from that in ordinary polymers and extends over longer time periods. One of the possible effects is a time-dependent behaviour that is not linked to viscoelasticity. The time scales for structural changes are then not related to any stress relaxation. This inelastic time-dependency is called thixotropy (Mewis, 1979).

#### 3.3.2. Reversible, heterogeneous changes in structure

When, during flow, the structural units grow to a sufficient size, they will start to affect the measurement results as discussed in section 3.1. This can also be the case when the structural units are individually much smaller but inter-

act over large length scales, essentially producing large, transient, percolating superstructures. This happens in flow-induced gelation, e.g. in some shear thickening suspensions. Depending on the case, gap size effects, wall slippage and/or an erratic response can be expected. The said structural changes require a minimum critical shear rate, the same holds for the corresponding measurement problems.

When the fluid consists of small molecules, the roughness of the wall at the atomic scale ensures the necessary momentum exchange with the fluid to avoid slip. Macromolecules, however, can be partially adsorbed on the wall and partially inbedded in the flowing liquid. When adsorption is inadequate, the macromolecules could be pulled off the wall during flow, thus generating slip. Other mechanisms for wall slip in polymer melts have been suggested, involving a.o. slip within the melt close to the wall. Real slip will depend on the intrinsic interactions between wall and polymer. Even chemical interactions cannot be excluded.

The presence of a wall might also be the source of other local changes. Wall-induced ordering can affect anisotropic molecules, determining the wall effect in liquid crystals. In suspensions with monodisperse spherical particles the wall could also cause a layered ordering which might affect the ordering in the bulk of the fluid. Flow, even without shear rate gradients (see later), can also result in segregation of components near the wall, producing again a slip layer. In suspensions this can be seen when the velocity is sufficiently high for particle inertia to become significant. The flow then exerts a net force on the particle, driving it away from the wall. As a result the layer near the wall becomes depleted in particles. In this manner a low viscosity layer can develop, giving rise to an apparent slip. Particle inertia could also cause radial concentration gradients because of centrifugal forces.

Reversible gels will not always start to flow evenly throughout the sample, no more than the plastic-like materials discussed sub 3.1. In addition to wall slip and shear bands, the gel might initially rupture as a solid, leaving a very heterogeneous structure that contains large pieces of unbroken gel. They gradually disappear at higher shear rates. Polymer or colloidal gels might also cause syneresis. A layer of expelled fluid develops near the wall, causing again wall slip.

### 3.3.3. Irreversible changes

Irreversible shear effects are not formally addressed within the theoretical framework of the rheological constitutive models but cannot be ignored in rheometry. The irreversible changes in rheological properties are often caused by flow-induced phase changes. In those systems that are not in equilibrium at rest, discussed sub 3.2, the changes that would also occur otherwise might be accel-

erated by the convective motion during flow. When the flow itself shifts the equilibrium, the resulting changes should be reversible (see 3.3.1). Irreversible changes arise when the material is in a pseudo-equilibrium state before the flow is applied and separated from the real equilibrium, or another, deeper, pseudo-equilibrium by a potential barrier. The latter should be large compared to the thermal energy of the structural units otherwise the structural changes would also occur at rest. If the flow is strong enough to generate hydrodynamic forces that can overcome the repulsive barrier, associations will be induced which remain after cessation of flow. Examples of this are provided by flow-induced crystallization of polymers and flow-induced aggregation in colloidal suspensions.

### 3.4. Shear rate gradients

In geometries as cone and plate or in a Couette with a narrow gap, the shear rate is nearly constant throughout the sample. This is not the case between rotating parallel plates or in flow-through rheometers. It is a basic assumption in normal fluid mechanics that this difference in flow field does not affect the intrinsic rheological behaviour. Hence the different geometries should produce the same material characteristics, at least for isotropic liquids, after all the necessary corrections have been applied. Slow or complex shear history effects might obscure the comparison. Occasionally, clear discrepancies between data obtained with different geometries have been reported. Some of these can be accounted for by structural changes induced by shear rate gradients.

The simplest case is that of suspensions. Without shear rate gradients particles might migrate away from the wall because of particle inertia as discussed sub 3.3.2. Shear will cause collisions between particles, creating a kind of osmotic pressure for the particles. When a shear rate gradient exists, there will also be a gradient of this pressure. The pressure being larger at the highest shear rates, a net migration towards regions with lower shear rates develops (Gadala-Maria and Acrivos, 1980; Leighton and Acrivos, 1987). The migration will stop when the concentration gradient balances the effect of the shear rate gradient. This type of particle migration also occurs in a normal Couette rheometer. Here, the shear rate is nearly constant in the gap between the cylinders but underneath the inner cylinder the fluid is only weakly sheared or even not sheared at all. During flow the particles will then slowly migrate out of the gap between the cylinders to this low shear zone. Avoiding the access to this layer by filling the lower part of the Couette with mercury eliminates the migration. Similarly, polymer molecules in solution could also migrate when a suitable shear rate gradient exists (MacDonald and Muller, 1996). Clearly, in capillaries wall-induced and gradient-induced migration will be superimposed.

## 4. Measurement procedures for complex fluids

Procedures for complex materials depend on the type of material and the instrument under consideration. The normal rules for selecting geometry and avoiding artefacts apply. Size of structural units should be considered with respect to gap size; migration, sedimentation, viscous heating, secondary flows and shear fracture should be avoided. Interaction with the environment, e.g. chemical reactions or evaporation, should be reduced as much as possible. Flow-through devices offer less possibilities than rotational devices to control the variables separately. Such devices are also less indicated for complex materials with very slow structural changes. For both groups of instruments either the driving force or a controlled motion can be applied. For complex materials this difference might become important. Even for ordinary polymer melts this is the case when studying the spurt phenomenon (Laun, 1998).

### 4.1. Flow-through devices

In flow-through devices length and gap size can be changed to determine entrance/exit effects and wall effects. It should be remarked that the normal correction procedures do not always apply. Bagley plots can become non-linear, a possible cause lies in the effect of pressure on viscosity and on density. The Mooney analysis for the wall effect does not hold universally either. In addition, time-dependent shear effects will interfere with entrance/exit effects. With slit dies, where pressure transducers can be mounted to measure pressure profiles in the die, these phenomena can be distinguished more easily. Irreversible ageing effects during the measurements that are not caused by shear can be detected by varying the residence time in the barrel before the actual measurement. Those changes that are induced by shear will show up when repeated measurements are performed with the same sample, after taking into account the ageing effects without shear. Wall effects and those caused by shear rate gradients are difficult to distinguish in this type of instruments. A comparison with different measurement geometries, e.g. sliding plates or cone and plate, could clarify this issue. Results that are independent of the measurement geometry are the most convincing evidence, although not absolute proof, for the physical relevance of the results.

### 4.2. Rotational devices

In rotational devices a number of problems can be studied more easily but other difficulties can arise, in particular because of the presence of a free surface. Shear fracture is often the most serious limitation. A slow decrease of the stresses above a critical shear rate (this might be just a few reciprocal seconds) is indicative for this artefact, observing the free surface of the material being the ultimate test. The stability of the sample, with and without shear, should also

be verified in rotational devices. It is, however, easier in such devices to control residence times and shearing times. Reversible, shear-induced changes in the material can sometimes be very slow, making it hard to distinguish them from irreversible changes. Even the superposition of measurements with increasing and decreasing shear rate or stress (hysteresis measurements) does not guarantee steady state behaviour for such materials. The presence of hysteresis does not imply really irreversible changes either. Sometimes recovering a particular structure requires submitting the sample to a more complex shear history, e.g. for polymer blends at low shear rates (Minale *et al.*, 1998).

Gap size effects can be detected but corrections for wall slip are more difficult in rotational devices. With a cone and plate correcting for a stress controlled slip velocity results in a varying shear rate in the sample, whereby the basic advantage of this geometry is lost. Using a parallel plate device in a squeezing mode has been suggested as a possible technique for studying wall slip in some materials (Laun, 1998). In the case of suspensions roughened tools can delay wall slip (see Fig. 1). This does not help when syneresis occurs in gels. The use of porous platens can then ensure wall anchoring.

### 4.3. Structure probing in complex fluids

A basic rheological characterization for a viscoelastic material includes at least measuring the steady state shear properties and the linear dynamic moduli. The possible difficulties involved in obtaining real steady state data have already been discussed. Dynamic experiments are not always trivial either. Normally it is automatically assumed that dynamic experiments probe the equilibrium structure at rest. In structured samples it might take a long rest period to reach this condition. The final structure might even be a pseudo-equilibrium, one that actually depends on the shear history prior to stopping the flow. In the same materials the linearity limit can be very low and various types of slip might cause erroneous results as well.

Transient measurements are very important for complex, structured materials. First of all these materials display more pronounced transients; they can be the essence of the rheological behaviour of the material, as in thixotropic samples. In addition, transients can be a very sensitive probe for structure, their characteristic shape can help to identify the nature of the structural changes. Interrupting the flow before a steady state has been reached and observing the subsequent stress relaxation offers a first possibility to study the instantaneous structure existing during shear at the moment shear was interrupted. This has been very successfully applied to polymer blends (Vinckier *et al.*, 1997). Alternatively, the response to a sudden change in shear rate can be used to probe structure during flow. In some cases, e.g. in liquid crystalline polymers, a flow reversal can be very instructive, especially in comparison with a sudden

increase in shear rate. In this manner the effect of the orientation of the structure, existing prior to the transient, can be evaluated.

To study the evolution of the structure at rest different techniques can be used. In thixotropic studies it has been customary to measure the start-up curve for the stress as a function of the rest period. This is by definition a destructive test. In principle measuring the linear dynamic moduli as a function of time provides a non-destructive test for structure recovery at rest. It should be borne in mind that the linearity limit normally decreases with increasing development of the structure. Hence the oscillatory motion, with a given peak strain, might gradually start to interfere with the structure recovery. This can be verified by checking whether using a smaller amplitude or only oscillating the sample intermittently affects the result. The evolution of the viscoelastic spectrum with time can provide useful structural information.

In principle, dynamic moduli could also be used to probe structure during flow. It requires that a small amplitude oscillation be superimposed on the steady state flow. This has indeed been used occasionally in the past, at present it can be performed with many stress-controlled rheometers. The oscillatory motion is then parallel to the steady state flow. In this manner the oscillatory flow is strongly coupled with the steady state motion and in general cannot be analysed as an ordinary oscillatory experiment without superimposed steady state flow (Vermant *et al.*, 1998). This problem is apparently not always understood. With a coaxial cylinder geometry the oscillation can also be in the transverse direction. The resulting superposition moduli are different from the parallel ones for nonlinear materials (Vermant *et al.*, 1998). A comparison between the two types of superposition is nontrivial but could be useful in testing constitutive equations. When the two types of moduli are compared without any superposed steady motion, they provide direct information about the anisotropy of the sample, even of its evolution in time.

It should also be mentioned that non-rheological measurements can provide detailed information about the interactions between flow, structure and rheology. Rheo-optical techniques are perhaps the most common ones, including in addition to classical flow birefringence the more recently introduced conservative flow dichroism. Furthermore dielectric spectra can be measured during flow, even as a function of time, and of course the various scattering techniques are now systematically used in flow situations as well.

## 5. Future developments

Although substantial progress has been made in commercially available rheological equipment, further developments are still possible. Temperature control is still not perfect in rotational rheometers and fast jumps in tem-

perature (e.g. for isothermal gelation studies) are nearly impossible. Measuring accurately normal stresses, especially transient ones, is also still a challenge. One of the consequences is that few laboratories can measure the second normal stress difference reasonably accurately. Having a controlled vertical motion allows both orthogonal superposition and squeezing flow measurements, this is now coming available. In normal oscillatory measurements the frequency range is usually limited, an extension to higher frequencies would be useful. Also rapidly determining the viscoelastic spectrum of changing systems is often necessary but not well implemented in commercial instruments.

Standard commercial instruments only measure the dynamic moduli corresponding to the basic frequency in the analysis of nonlinear oscillatory behaviour. In this manner substantial information about the nonlinearity is lost. With techniques like the Fast Fourier Transform this additional information could be made available. It can be used to discriminate between different kinds of structure or material.

An even more important development in rheometry would be to include flows other than simple shear flow. Extensional rheometers are slowly emerging on the market, but could be improved. Higher extension rates, a variable and controlled flow history as well as more homogeneous deformations should be very important in this respect. Flows beyond simple shear flow are relevant because industrial processes involve more complex flows. In addition such flows are often more sensitive to minor differences between materials. Simple analytical solutions cannot be applied to the measurements anymore in that case but simulations could provide material characteristics. The opposed jet rheometer has been used in this manner (Purnode and Crochet, 1996). This new development is sometimes called computational rheometry. The use of simulations implies that a specific rheological model has to be used, which is a limitation of this approach. An other possible extension would be to measure the velocity and stress fields in complex flows to extract rheological information. Up to now such set-ups have been used to evaluate rheological models. No attempts have apparently been made to optimize the geometry for rheological measurements.

In recent years other techniques have been increasingly combined with rheological measurements, either simultaneously or in parallel under identical flow conditions. This is expected to increase in the future as interest and insight in the underlying microstructural mechanisms is growing.

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