Chapter 7 Questions

1. Name three (or more) experiments that can be used to assess thixotropy.
2. Explain the hysteresis loop of thixotropic systems in the stress versus shear rate curve when gradually increasing and decreasing the shear rate.
3. Describe an experiment with which thixotropy can be distinguished from ordinary viscoelasticity
4. A constant stress, higher than the dynamic yield stress is applied until a steady state has been reached. Subsequently, the stress level is suddenly reduced to a level smaller than the dynamic yield stress. Discuss the corresponding evolution of the viscosity.
5. What general types of constitutive equations are commonly used to describe thixotropy?
6. What physical mechanisms does one have to include in a kinetic expression for the structure parameter of a weakly flocculated, thixotropic system?
7. Describing the microstructure of a flocculating, thixotropic suspension by a scalar parameter implies a substantial, sometimes unphysical, simplification. Provide examples that confirm this statement.

Chapter 7 Answers

1. Experimental techniques that can be used to estimate thixotropy include: a) measurement of the overshoot viscosity when starting up the shear flow after different rest periods and plotting the overshoot viscosity as a function of rest time; b) a hysteresis loop in which the shear stress is measured while gradually increasing the shear rate at a constant rate up to a maximum value, and then decreasing it at the same rate; c) tracing the transient viscosity for a step change in the shear rate or shear stress; d) measuring the time evolution of the dynamic moduli in small amplitude oscillatory flow after previously shearing the sample.

2. When increasing the shear rate at a constant rate (ramp), the stress will normally also increase. If the shear rate increases fast enough the microstructure and the stress never reach their steady state value at a given shear rate: they lag behind. Because of this lag they are above their steady state values. When, after reaching its maximum value, the shear rate is being reduced at the same ramp rate as during the increase, the structure will again lag behind its steady state value because now it cannot build up fast enough. At this stage, lagging behind means being below the steady state value, which then also applies for the shear stress. As a result the shear stress at each shear rate level will be higher when going up than when going down. Hence, plotting shear stress versus shear rate results in a hysteresis loop with the increasing part above the decreasing part. Note that more complex behaviors can be observed.

3. The difference between thixotropy and normal viscoelasticity shows up when applying a stepwise decrease in shear rate. In this experiment, the initial shear rate is applied until the steady state is reached. The stress is then suddenly decreased and the resulting, transient viscosity is recorded. In case of an ordinary viscoelastic fluid this experiment will result in a gradual relaxation of the stress to the steady state level at the lower shear rate. At sufficiently high shear rates, ~~As~~ the thixotropic system is dominated by hydrodynamic interactions and so,~~,~~ the stress will drop immediately upon reduction in the shear rate as the hydrodynamic stress is proportional to the shear rate. With a thixotropic system the structure requires time to evolve to the value consistent with the new shear rate (build-up). Thus, immediately after the step down in shear rate, the structure is below that for the steady state and consequently, the viscosity will instantaneously be lower than for the steady state value. Thus, the viscosity and stress will increase with time after the step down as the structure builds up- the opposite behavior as for the viscoelastic system. . If there is some elasticity in the thixotropic system, a similar decrease in stress will be observed prior to the increase due to structure rebuilding. In most practical cases the viscoelastic relaxation is faster than the structure rebuilding stage.

4. The particulate network structure responsible for the yield stress is broken down by the application of stress. Upon a step-down in stress, the structure initially is in this

broken-down state. Hence, the sample can still flow at a stress below the equilibrium yield stress. However, the structure will gradually evolve towards its steady state level, which initially results in a gradual increase in viscosity. The growing viscosity causes the motion to slow down, which in turn will accelerate the building up of structure and viscosity. Therefore the viscosity increases at a continuously growing rate. As the steady state viscosity is infinity at this stress level (which is below the dynamic yield stress) the viscosity will in the end diverge to infinity and the sample will stop flowing.

5. In a micromechanical approach, the evolution of the microstructure during flow is described by means of basic equations describing the underlying mechanisms by which structure is broken down by flow, reformed by flow and other processes, such as Brownian motion. The stresses are then calculated from an additional equation that links the microstructure and the given flow conditions to the stresses.. A more phenomenological approach is normally inspired by a simplified and more general picture of the microstructure and its evolution as a function of the flow history. In this approach, the level of microstructure is commonly expressed by a scalar structure parameter. A general rheological model is selected and its parameters are written as functions of the structural parameter. To generate a thixotropy model an evolution equation for the structural parameter has to be added. For this purpose the same two methods can be used as are typically employed in the theory of viscoelasticity. One can either write a differential equation that describes the instantaneous rate of change of the structure parameter as a function of the instantaneous kinematics or, alternatively, one can link the structure parameter to the shear history by means of an integral memory function.

6. Three mechanisms for changing the structure can be distinguished. Firstly, the microstructure can be destroyed by hydrodynamic forces. Secondly, it can grow as a result of Brownian motion and the formation of new bonds between particles when attractive interparticle forces exist. Finally, in addition to Brownian motion weak flows flow can also induce flocculation by bringing particles together

7. The structure consists of flocs, either isolated or assembled into a network. Using a single scalar parameter presupposes that evolution of size, as well as shape and internal structure of the flocs, could all be described by a single parameter. This parameter should also cover the evolution of a percolating network. If the flocs are fractal and the fractal dimension remains constant, the internal structure is not affected, but this is not always the case as compaction of flocs can occur during flow. Anisotropy in the microstructure cannot be described by a scalar order parameter, and this is apparent in flow reversal experiments, where a dip and recovery in the viscosity is often observed whereas the scalar structure parameter does not change upon flow reversal.