On the viscosity and rheological properties of polymer gels

Theoretical background: Thomas G. Mezger: *The Rheology Handbook*, Vincentz Network, 4th Edition.
Type of practice: Single.
Aim of practice: To investigate the structure formation and rheological properties of gels.

1 Introduction

1.1 Macromolecular gels

Nowadays, different polymers are widely used in applications (e.g. cosmetics and personal care products, essential components of drug delivery vehicles, etc.). The viscosity of creams and pastes are frequently adjusted by adding various polymers. They are even applied to modify the delivery and release of drugs.

Macromolecules are giant molecules which are built up from a large number of repeating units (i.e., monomers) linked by covalent bonds. Their relative molecular mass (M_r) is usually above 10 000. Their chemical structure shows a great variability (e.g. linear or cross-linked molecular chains, different functional groups, etc.) and thus their properties do so as well. Macromolecules can be dissolved in appropriate solvents, but the solubility dramatically decreases with growing molecular mass. Compared to the small molecule materials, polymers typically dissolve very slowly. The solvent molecules penetrating into the solid particles solvate (in water hydrate) the molecule chains. The volume of the particles grows, i.e., they swell, and the swelling turns *unlimited*. At this stage the solvated chains become free and the individual polymer coils move away in the solution. By the end, *colloidal solution* forms in which the macromolecules exhibit a homogeneous spatial distribution.

If the swelling of water soluble macromolecules is not *unlimited* under the conditions (e.g., appropriately high concentration), hydrogels form with 3-dimensional polymer network. Water hydrates the molecule chains building up the gel skeleton, functional groups dissociate / protonate and the forming charges repel each other. Natural gelling agents (e.g., chitosan, hyaluronic acid, and cellulose derivatives such as carboxymethil-, hydroxyethyl-cellulose) are frequently used in pharmaceutical formulation, cosmetics, and food industry.

Biopolymers typically insoluble in water can be chemically treated in order to obtained hydrogel forming agents (e.g. oxidation, hydrolysis, ether and ester derivatives, etc.). A good example is the carboxymethyl-cellulose (CMC, Fig. 1), which is an anionic polyelectrolyte made of cellulose by chemical treatment. The carboxymethyl ($-CH_2-COO^-$) functional groups of polysaccharide chains composed of β-D-glucose units significantly increase the water solubility of cellulose, thus it can be used in food and pharmaceutical industry as emulsifier and volume enhancer. The relative molecular mass of CMC can even reach 100 000. In contact with water, CMC swells rapidly and forms hydrogel at relatively low concentration.

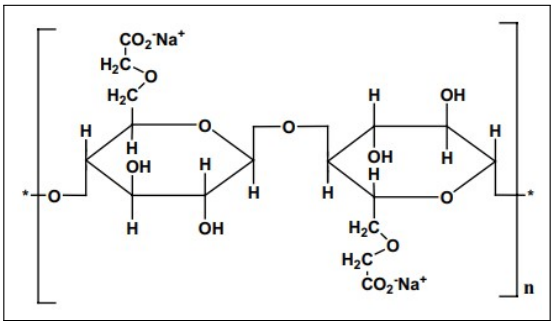

Figure 1: Structural formula of CMC.

By their structure, we classify the water soluble macromolecules as:

- non-ionic macromolecules, which are hydrophilic polymers frequently containing hetero atoms in the chain (e.g. polyethylene oxide, polyethylene glycol (PEG)), and

- ionic macromolecules or so called polyelectrolytes, which contain chemically bonded functional groups which can undergo dissociation / protonation, thus can become locally charged.

According to their functional groups, polyelectrolytes can be anionic (i.e, acidic, e.g., $-\mathrm{COO}^-$, polyacrylic acid), cationic (i.e., alkaline, e.g. $-\mathrm{NH}_3^+$, polyethyleneimine), and amphoteric (e.g., proteins and gelatin). Their overall charge depends on the functional groups, on the *p*H of the medium, and on the type and concentration of other electrolytes in the system. Upon dissociation / protonation of the functional groups, the polymer coils achieve a net charge which is neutralized by counter ions. These effects influence the conformation of unique polymer coils and thus the viscosity and rheological properties of polymer solutions and gels.

1.2 Viscosity

Viscosity, or so called internal friction measures how much a fluid (gas or liquid) stands against the shear stress (or drag) which would make the fluid move.

The flow field within a tube (capillary) is illustrated in Fig. 2. Laminar flow evolves provided that the flow rate is not too high. This can be imagined as a medium divided into infinite number of coaxial cylinders moving parallel with respect to each other. The motion of fluid particles on the microscale is parallel to the macroscopic flow direction, thus the layers cannot mix with each other. However, the propagation velocity of the coaxial layers depends on the distance to the boundary (e.g., to the tube wall; see the different lengths of black arrows in Fig. 2). Provided that the motion of the coaxial cylinder layers is parallel and steady, the internal friction force opposing the motion (F) is linearly proportional to the area of the slipping layers (A) and to the velocity gradient (or shear rate γ; in two dimensions, considering the longitudinal cross section of the tube: du/dy, i.e., to the change of flow velocity per unit distance). The proportionality factor characteristic to the given fluid is its dynamic viscosity (η):

$$\mathrm{F} = \eta\,\mathrm{A}\,\frac{\mathrm{du}}{\mathrm{dy}}. \tag{1}$$

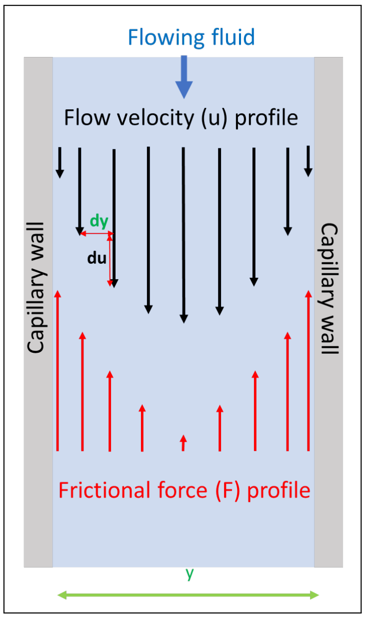

Figure 2: Flow profile in a tube (capillary).

Introducing $\mathrm{F}/\mathrm{A} = \tau$ shear stress and $\mathrm{du}/\mathrm{dy} = \gamma$ notations:

$$\tau = \eta\gamma, \tag{2}$$

which is known as the Newtonian law of viscosity. It validly describes the behavior of so called Newtonian fluids (gases and liquids of small molecules). However, the viscosity is not constant for many materials, i.e., τ is not a linear function of γ. In this case τ/γ is called the apparent shear viscosity (η_γ). SI unit of τ is N/m^2, which is frequently called Pa, however, it is not a pressure (since the force is not perpendicular to the surface) but a stress (because the force is parallel to the surface). SI unit of γ is velocity/distance, i.e., $(\mathrm{m}/\mathrm{s})/\mathrm{m} = \mathrm{s}^{-1}$. Hence the unit of dynamic viscosity is $\mathrm{Pa}\cdot\mathrm{s}$.

1.2.1 Rotational viscometry

The sample is placed between two coaxial cylinders in rotational viscometers. One cylinder is stationary, and the rotation of the other one can be adjusted to different angular velocities (left panel of Fig. 3). The rotation of the inner cylinder tangentially shears the sample, which thus exerts a resistance against the deformation force, i.e., a frictional force rises.

Under appropriate conditions the flow is laminar, because the liquid sample in between the two cylinders can be considered as infinite number of coaxial and cylindrical liquid layers rotating on each other (i.e., the

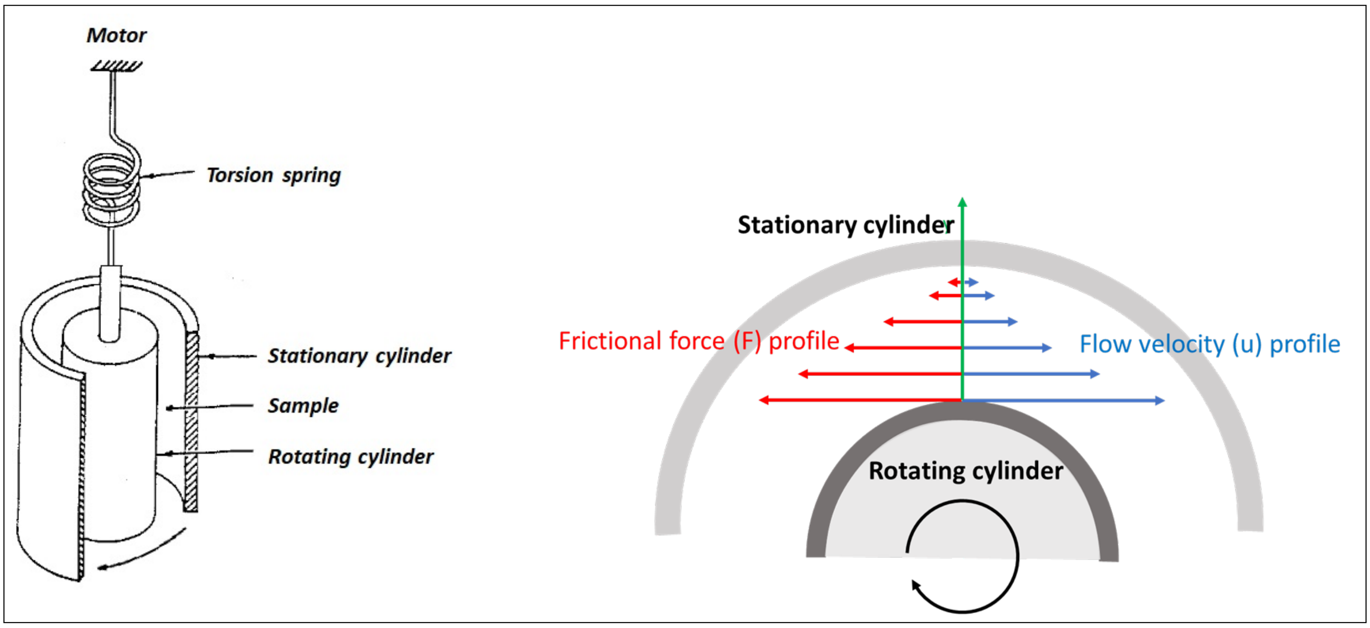

Figure 3: Sketch of a rotational viscometer (left) and the evolving flow field (right).

neighboring layers now do not pass by each other longitudinally as shown previously in Fig. 2). Similarly for the pipe flow above, under laminar flow conditions the friction force F is linearly proportional to the surface of the cylinders (A) and to the shear rate (du/dy). This force (or rather the shear against what this force rises) is *measured* via the elongation of the torsion spring (i.e., how much the spatial delay is between the rotated cylinder and the rotating engine shaft). Liquid molecules in contact with solid surface adheres to the surface and do not flow. Therefore the liquid layer attached to the rotating cylinder moves with its peripheral velocity, while the liquid layer attached to the stationary cylinder is still (length of arrows in Fig. 3, right panel). Thus the shear rate (D) can be determined as the ratio of the peripheral velocity of the rotating cylinder ($u_{\text{periphery}}$) and the distance between the two cylinders (b). The peripheral velocity can be adjusted by the rev of the engine (ν), thus

$$D = \frac{du}{dy} = \frac{u_{\text{periphery}}}{b} = \frac{(2r\pi)\,\nu}{b}, \tag{3}$$

where r is the radius of the rotating cylinder. Given a pair of rotating and stationary cylinders, the instrument calculates the value of γ from known ν and b.

Similarly to that presented for a laminar flow in a capillary in Section 1.2, upon introducing $F/A = \tau$ shear stress

$$\tau = \eta\gamma,$$

where the proportionality factor characteristic to the given fluid is its dynamic viscosity (η). As mentioned above, this equation is only valid for Newtonian fluids (gases, liquids of small molecules), where η is constant. However, numerous and practically relevant system behaves differently. For non-Newtonian fluids η is a function of shear rate (i.e., τ is not a linear function of γ). τ/γ fraction is called apparent shear viscosity (η_γ). The following empirical law describes many systems (non plastic, non thixotropic):

$$\tau = K\gamma^n, \tag{4}$$

that is, the shear stress is a power function of shear rate. The numerical value of coefficient K is the dynamic viscosity (η) for Newtonian fluids ($n = 1$), otherwise it is the apparent viscosity ($\eta_{\gamma=1/s}$) belonging to unity shear rate ($\gamma = 1/s$). The unit of K is $\text{Pa}\cdot\text{s}^n$. *Fitting parameters* K and n can be applied to compare the rheological behavior of various polymer systems (flow and viscosity curves).

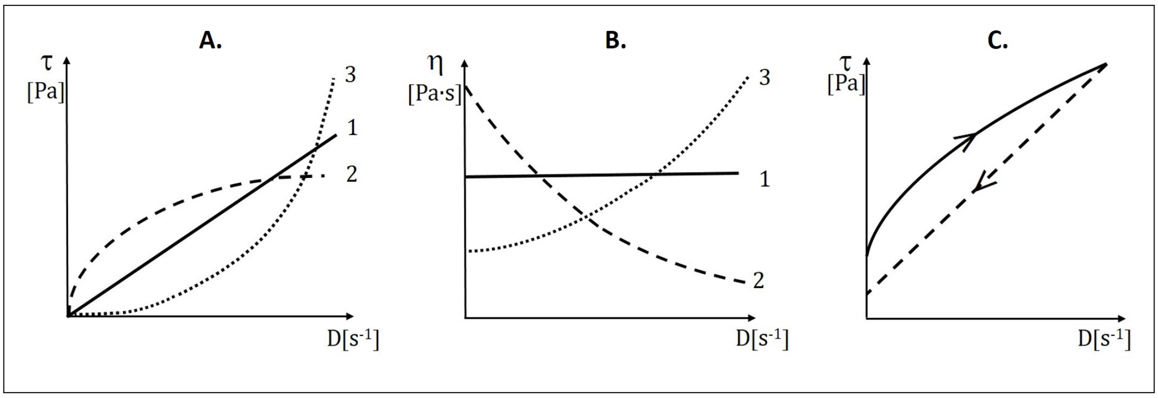

Figure 4: Flow (A) and viscosity (B) curves of various rheological systems; flow curve of a thixotropic system (C). 1: ideal viscous (Newtonian); 2: pseudoplastic (shear thinning); 3: dilatant (shear thickening).

1.2.2 Non-Newtonian polymer systems

Rheology focuses on the deformation or flow induced by an external force on the sample body. The most frequently applied deformation is the shear, when the force tangentially acts on the body surface. We distinguish three different ideal behaviors from the perspective of rheology: ideal elastic (its shape deforms due to the acting force, but returns to the initial state when the force vanishes), ideal viscous (its deformation is proportional to the shear), and ideal plastic (its shape deforms due to the acting force, and will stay unchanged even if the force vanishes). Most (real) materials show an intermediate behavior in between those ideal ones. Under appropriate conditions (not too dilute polymer solution and relatively small electrolyte concentration), polymer systems are viscoelastic, i.e., their mechanical and rheological properties are between elastic solid and viscous liquid states.

The viscosity of polymer solutions depends on the temperature, the chemical character of the solvent, and on the type (including the molecular mass) and concentration of the polymer. Rotational viscometry is the best method to study the flow properties of not too dilute (i.e., exhibiting non-Newtonian behavior) polymer solutions and gels, suspensions, and other colloid systems.

There are two deviations from the ideal (Newtonian) behavior:

- shear thinning (pseudoplastic), i.e., the apparent shear viscosity (η_γ) decreases with the increasing shear rate ($n < 1$ in equation (4); curves no. 2 in Fig. 4; e.g., ketchup, blood, lubricants),
- shear thickening (dilatant), i.e., the apparent shear viscosity increases with the shear rate ($n > 1$; curves no. 3 in Fig. 4; e.g., corn starch suspended in water, sand completely soaked with water).

It must be noted that, even though n is independent of shear stress (i.e., independent of shear rate γ when applying a given cylinder pair for the rotational viscometer), it depends on the polymer concentration. If the value of n approaches 1 when the concentration is changed, then the system approaches Newtonian behavior within the investigated concentration regime. The contrary is true as well: large deviation from $n = 1$ reflects a non-Newtonian behavior. Therefore, the flow properties of such systems cannot be simply characterized by a single value (i.e., by the apparent shear viscosity η_D measured at a given shear rate). Indeed, $\tau = f(\gamma)$ flow curves and $\eta = f(\gamma)$ viscosity curves are to be registered (Fig. 4).

There are such systems (pastes, creams, gels), whose viscosity depends both on the magnitude of the exerted force and on the length of the impact time. This behavior can be measured and characterized if the relaxation time of the system falls within the measurement time ($10-10^3$ s). The most prominent time-dependent phenomena:

1. Thixotropy, when the self-sustained structure of the sample builds up while standing still (which may need short or long time depending on the system), whereas it rapidly collapses upon mechanical stress (e.g., shear) and the sample flows. The process is reversible; when the shear diminishes, the sample regenerates to solid-like state. This reversible sol–gel transition is characterized by the thixotropic loop

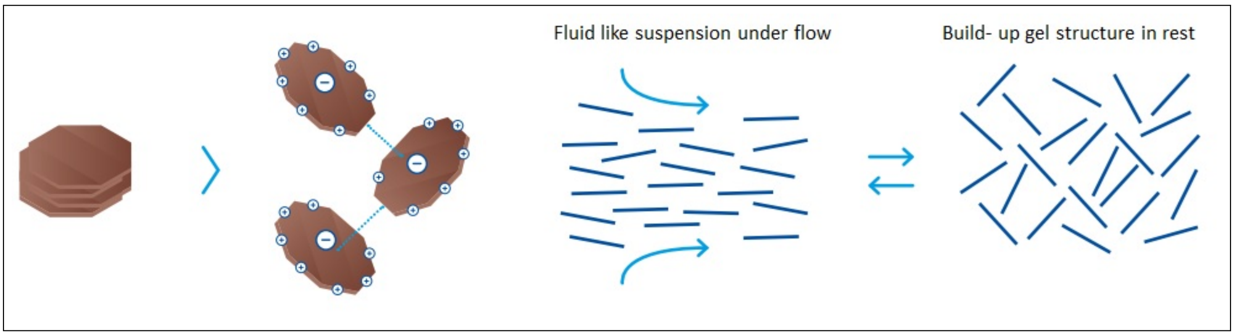

Figure 5: Schematics of clay mineral lamellea, and the behavior of the suspension under shear stress and without it.

(Fig. 4C). This phenomenon is observed, e.g., for many clay mineral suspensions. These materials own such layered structure, where the surface of the separate lamellae is negatively charged, while their edges are positive. Therefore, due to the electrostatic interactions, a house of cards structure builds up in still (gel-like) state, which collapses when shear sets in (Fig. 5). Due to this property, natural (e.g., montmorillonite) and artificial (e.g., Optigel) phyllosilicates are frequently applied in oil (e.g., drilling mud) and cosmetics industry (e.g., creams and pastes) to set the viscosity and maintain thixotropic characteristics.

2. The opposite behavior is called anti-thixotropy.
3. Finally, rheopexy is the rare behavior when the structure builds up during slow stirring.

2 Experimental

2.1 Flow and viscosity curve measurements of non-Newtonian hydrogels by rotational viscometry

Using the CMC stock gel, prepare a dilution series of 5 samples, where the mass concentration changes equidistantly within the given range. The concentration range of the gel samples is denoted by the instructor. *If the instructor does not state otherwise*, the two extrema are 2.5 and 20 g/l. Register the apparent shear viscosity of the samples at different shear rates.

1. Prepare the dilution series of 5 samples according to the given concentration range. The planned mass concentrations and aimed gel volumes must be checked by the instructor. Measure the appropriate volume of the CMC gel into a 50 cm^3 beaker and add the right amount of water to achieve the aimed concentration in 25 cm^3 total volume. Homogenize the sample with a glass rod. Do not stir rigorously otherwise bubble inclusions may appear. The system is homogeneous if the motion of regions with different refractive index is not seen.
2. Prepare an other sample at will according to the previous recipe with the restrictions that its mass concentration must be in the range of 10 and 20 g/l and it is not identical with any previous samples. This sample is called *unknown* henceforth.
3. Set the rotational viscometer according to the information in the Supplementary Materials.
4. Perform the measurements according to the information in the Supplementary Materials. Measure the most dilute sample first, and then in the order of increasing concentration.

2.2 Investigation of the thixotropic properties of clay minerals via rotational viscometry

The aim of this part of the practice is to characterize the thixotropic property of a clay mineral suspension (Optigel). By applying the 20 g/l Optigel stock sample, prepare a dilution series of 3 samples with 10, 15 and 20 g/l mass concentration according to the recipe described for CMC hydrogel. Register the flow curves of the sample first during ascending, then during descending shear rate within the range previously given by the instructor. To measure the apparent shear viscosity at decreasing shear rates, swap the starting and final shear rate values according to point (h) in the Supplementary Materials. This way the instrument will register the curve along decreasing shear rate. Perform the measurement on the Optigel stock sample and for its three dilutions.

3 Evaluation of the measured data

3.1 Flow and viscosity curve measurements of non-Newtonian hydrogels

1. Summarize the measured data for the separate measurements according to Table 1.

   Table 1: Results of rotational viscometry.

   $c_{\mathrm{CMC}} = \ldots$ g/l

γ / s^{-1}	τ / Pa	$\eta / \mathrm{Pa{\cdot}s}$

2. In two separate graphs, plot the flow and viscosity curves of the gels of different concentrations. *For preparing the graphs, use a software which you will apply for points 3 and 4 of the evaluation.* Explain the curves' tendencies and characterize the rheological behavior of the investigated hydrogel. How and why the concentration of the polymer gel influences the curves?
3. *Important notice: Do NOT perform this step for the „unknown" sample.*

   Prepare a graph containing data for each concentration applying equation (4). *According to the instructor's request*, use either the linearized form ($\lg(\tau / \mathrm{Pa}) = \lg(\mathrm{K}) + n \lg(\gamma / \mathrm{s}^{-1})$) or perform nonlinear parameter fitting (see Appendix; Excel Trendline: power law, Origin, QtiPlot, etc.). If nonlinear parameter fitting is requested, no need to prepare a new graph, the one prepared for the previous point of the evaluation is applicable. If the linear equation will be used, add two extra columns to Table 1 ($\lg(\gamma / \mathrm{s}^{-1})$ and $\lg(\tau / \mathrm{Pa})$) and use them for the plot and fitting.

   Summarize the fitting parameters according to Table 2.

   Table 2: Concentration dependence of the fitting parameters of CMC.

c_{CMC} (g/l)	$\mathrm{K} / \mathrm{Pa{\cdot}s^n}$	n

4. Plot K and n values against CMC mass concentration in a common graph; use separate y-axes. Explain the trends. If possible, linearly fit the concentration dependence of n values, while fit a power function ($y = a \cdot x^b$) for that of K values; give the equations of the empirical calibration curves.

5. By applying the equations of the above calibration curves, calculate the values of K and n for the mass concentration of the *unknown* sample. With those values in hand, plot the calculated flow curve of the *unknown* sample in between the already existing graph of flow curves (i.e., define a function with known K and n values according to the right form of equation (4)). Compare the measured and calculated flow curves of the *unknown* sample and explain the similarities and differences.

3.2 Investigation of the thixotropic properties of clay minerals

1. Summarize the measured data according to Table 3 for each concentration. Plot the flow curves of the clay mineral suspensions registered during ascending and descending shear rate values in a single graph. If possible, plot the curves of each concentration in a single graph (i.e., if the curves do not overlap so they can be inspected separately). Otherwise, prepare separate graphs for each concentration. How and why the concentration of the suspension influences the trend of the curves?

Table 3: Results of Optigel rheological investigation.

$c_{\text{Optigel}} = \ldots$ g/l

$\gamma\,/\,\mathrm{s}^{-1}$	$\tau_{\text{ascend}}\,/\,\mathrm{Pa}$	$\tau_{\text{descend}}\,/\,\mathrm{Pa}$

2. Determine the area of the thixotropic loop for each concentration. To do so, numerically integrate the registered flow curves applying any method (see Supplementary Materials II). If requested by the integration method, add extra columns to Table3.
3. Plot the area of the hysteresis loop as a function of the mass concentration of the clay mineral suspension and explain the trends.

Questions

1. What kind of macromolecules are able to dissolve in water and which can only swell? List 1–1 example.
2. What is Newtonian liquid? List two examples.
3. What is shear stress? (definition, notation, unit)
4. What parameters influence the viscosity of polymer solutions and what is the typical difference between the viscosity of macromolecular and regular (small molecules) solutions?
5. What kind of materials must be rheologically characterized? What is flow curve and what is viscosity curve? List the flow curve types you know.
6. List the basic deviations from Newtonian behavior of liquids and provide 3 example liquids.
7. What is the thixotropy? Sketch the corresponding flow curve and name one example.
8. Briefly describe how rotational viscometer works.
9. How to prepare 25 cm^3 of 3 g/l CMC gel from the available 30 g/l CMC gel?
10. When the flow curve was registered for an Optigel sample, you obtained the shear stress – shear rate data set summarized in the table below. By applying numerical integration based on the trapeziodal rule, calculate the integral of the corresponding $\tau(\gamma)$ function on an interval whose limits are selected by you. (The limits must be consecutive shear rates of the table.)

τ / Pa	1499.6	1481.1	1462.2	1443.2	1424.3	1405.4	1386.5	1367.5	1348.6
γ / s^{-1}	125.6	118.5	115.8	114.0	112.9	111.4	110.5	109.3	108.4

Supplementary Materials I:

Brookfield RST-CC rotational viscometer

Important notice! Due to the vulnerable nature of the torsion spring, the rotational viscometer is a very sensitive instrument which must be handled with special care. When you insert or remove the spindle (i.e., to rotating cylinder) for the first time, ask for the assistance of the instructor. Either the instructor or the technician will check on the condition of the spindle, engine shaft, and torsion spring at the end of the practice. The student is financially responsible for the instrument, any damage caused by inappropriate use will come with a repair cost (e.g., if the spindle falls down and its shape deforms, it could not be used anymore for the measurement and a new spindle must be purchased).

Brookfield RST-CC rotational viscometer is designed to determine the dynamic (and / or apparent shear) viscosity of the sample, i.e., to observe how the sample behaves when a force deforms it.The SI unit of dynamic viscosity is Pa·s. In a rotational viscometer, the spindle is linked to the engine shaft via a torsion spring. During the measurement, the sample exerts a resistance against the rotating motion of the spindle, thus causes an angular delay of the spindle in comparison to the engine shaft (i.e., the elongation of the torsion spring). This delay is proportional to the viscosity of the sample. The shear stress exerted on the sample between the stationary and rotating cylinders is proportional to the shear rate and the surface of the spindle. Therefore, by adjusting the parameters (i.e., the rev of the engine and the type of the spindle) one can determine the dynamic (and / or apparent shear) viscosity of the sample in a wide range.

1. **Inserting / removing spindle**
   The engine shaft of the instrument is protected by a white lid and a gray foam rubber against any mechanical damage. The lid and the foam rubber must be kept on the shaft when the instrument is not in use. The appropriate condition of the engine shaft is checked by the instructor before and after the measurement. Insert the spindle carefully as detailed below:

   (a) Wind-off the black screw-ring (together with the white lid in it) and remove the gray foam rubber. The screw-ring (after the white lid is removed from it) will be used later to fix the sample holder thus keep it close to the instrument.
   (b) Gently and fully (ca. 0.5 cm) lift up the black fast connector located at the tip of the engine shaft (it moves easily) and keep it up. At this position you will see the bearing balls at the end of the engine shaft.
   (c) Insert the CCT-25 spindle and pull down the fast connector. Before you let off the spindle, gently pull it downwards to check if the hanging is stable.
   (d) To remove the spindle, hold it with one hand and lift up the fast connector with your other hand. Then you can fully remove the spindle.

2. **Executing a measurement**

   (a) Turn on the instrument with the button on its back.
   (b) Start the measurements with the most dilute (i.e., less viscous) sample. Fill in ca. 15 – 20 cm^3 sample into the MBT-25 metal sample holder (the sample must overcome the circular sign inside the sample holder). Once the appropriate spindle is connected to the shaft, slowly and carefully slip up the sample holder around the spindle (avoid any friction between the two objects). Without letting off the sample holder, fix it to the instrument body with the screw-ring. If possible, double check that the sample meniscus overcomes the upper surface of the spindle, thus the sample fully occupies the measuring hole between the two cylinders.
   (c) Select *Run Single* on the LCD screen.
   (d) Select *Wait for Temperature* in the *Temperature option* menu and push *OK*.
   (e) Set the laboratory temperature and push *OK*.

   (f) The instrument automatically recognizes the already inserted CCT-25 spindle, thus select *Recognized Measuring System* and push *OK*. (If the instrument did not recognize the spindle, select *CCT-25* in the upcoming *Measuring System* menu and push *OK*.)
   (g) Select *Shear rate* (γ) in *Experiment type* menu and push *OK*.
   (h) Set the final and starting values of shear rate. *If the instructor does not state otherwise*, these should be 1500 and $5\,\mathrm{s}^{-1}$, accordingly; then push *OK*.
   (i) Set the measurement points and time in *Measuring point and time* menu. *If the instructor does not state otherwise*, these should be 80 points and 120 s.
   (j) Name your file in *Substance (sample material)* menu. Give such names which help you later to recall file contents (avoid special characters, e.g., space, $, :, ., &, etc).
   A possibility: *Givenname-Surename-ZZ-DDMMYYYY*, where *ZZ* is the gel composition and, *DDMMYYYY* is the date. When the file name is accepted, the measurement automatically starts.
   (k) During the measurement, the instrument displays in real time how the shear stress (τ) and viscosity (η) change with shear rate (γ). Once the measurement is over (*finished*), you may select the *Graph* icon to oversee the registered curve. It is a good choice to check the measured curve this way before you waste the investigated gel sample.
   (l) At the end of the measurement, return to the main menu (🏠 icon in the upper corner) with ⇥ icon. Then, slowly and gently remove the sample holder from the spindle (avoid any friction of the bodies) an let the gel drop off the spindle. While holding the spindle, loose the fast connector and remove the spindle. Wash and rinse the spindle and the sample holder (this latter one has a removable bottom cover for more comfortable cleaning).
   (m) Repeat points (b)–(l) to perform the measurement for all samples.
   (n) At the end of the very last measurement, act according to point (l), and place the clean and dry spindle and sample holder into their packaging.

3. **Exporting measurement data**

   (a) Plug in the USB stick (which belongs to the laboratory equipment) into the USB extension wire. (You should not use your own USB drive.)
   (b) Once the USB drive is recognized (green ⭍ sign in the upper menu bar), select *Settings* icon in the main menu, then select *Memory* icon.
   (c) Double click on 🔍 icon and select *DATA 2* folder.
   (d) Designate your measurement files and click on *Data transfer icon*. Although the file names were set prior each measurement, those names do not appear here; in this menu you can navigate based on the date and time of the files. The file names bear with importance later to be able to review the applied concentrations. For some reason, you cannot mark at will a number of files for copy; the best choice is to copy such amount of files which are displayed on the screen at once. When the *Please wait, copying in progress* message disappears, simply unplug the USB drive from the extension wire; there is no possibility to unmount the drive as a regular process for PCs. The measurement data can be copied from the USB drive using the PCs of the Education Level. Either copy the data to your data drive or send them via e-mail; you cannot take home the provided USB drive.

4. **Finally, turn off the viscometer on the back, place back the foam rubber and wind-on the screw-ring with the white lid in it.**

Supplementary Materials II:
Numerical integration

There are several ways to numerically calculate the area A under a function $f(x)$ determined by a set of measured data (i.e., the area surrounded by the function and the independent variable (x-axis)) on an interval $x = [a,\, b]$.

Numerical integration based on Netwon–Leibniz axiom: When applying this method, we plot a function through the measured data, then we calculate the area under the function by integrating according to Netwon–Leibniz axiom (Fig. 6, left panel). If the theoretical equation of the plotted function (i.e., its physicochemical interpretation) is not known, and the measured data can be considered as a part of a continuous function, then one may try to fit a polynomial (see appendix). In this scenario

$$f(x) \approx \sum_{i=0}^{n} c_i x^i\,, \tag{5}$$

where c_i is the coefficient of x on different powers; taking a second-degree polynomial as an example $f(x) = c_2 x^2 + c_1 x^1 + c_0 x^0$. The primitive function of it (indefinite integral, $F(x)$) is calculated as:

$$F(x) = \int f(x)dx = \sum_{i=0}^{n} \frac{c_i}{i+1} x^{i+1}\,, \tag{6}$$

which is $F(x) = \frac{c_2}{3}x^3 + \frac{c_1}{2}x^2 + \frac{c_0}{1}x^1$ for the second-degree example polynomial. The area A (definite integral) is then obtained on $[a,\, b]$ interval as

$$A = \int_a^b F(x) = F(b) - F(a)\,, \tag{7}$$

that is, first the upper limit (b) then the lower limit (a) is substituted into x in equation (6), and then we subtract the two terms from each other. For our example function

$$A = \frac{c_2}{3}b^3 + \frac{c_1}{2}b^2 + \frac{c_0}{1}b^1 - \left(\frac{c_2}{3}a^3 + \frac{c_1}{2}a^2 + \frac{c_0}{1}a^1\right)\,.$$

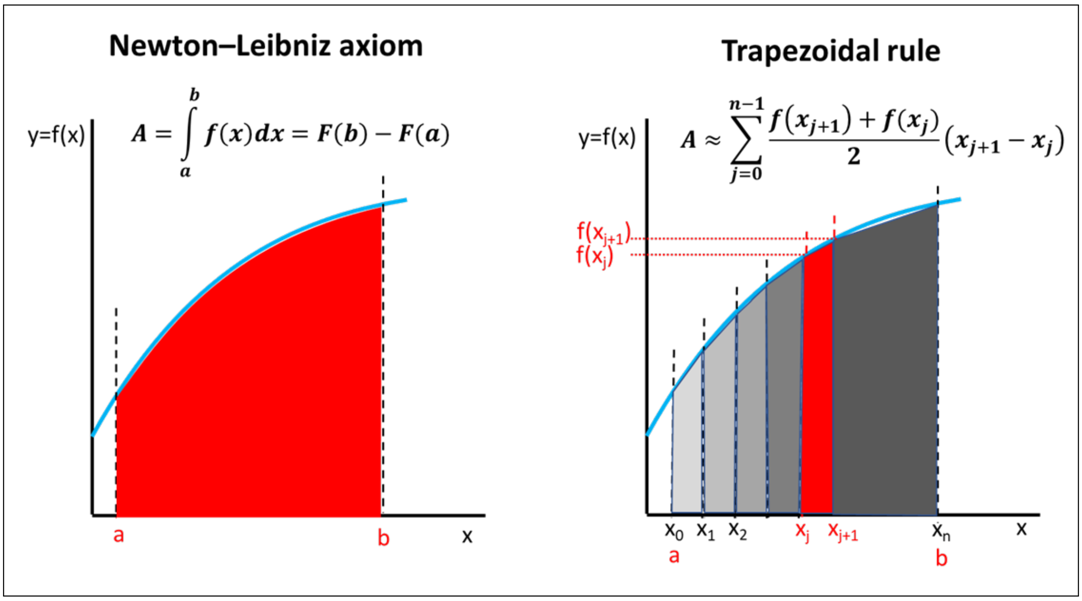

Figure 6: Determining the area under a function by numerical integration.

Numerical integration based on trapezoidal rule: This method approximates the integral (the area A under the measured curve, see Fig. 6, right panel) with the sum of the areas of finite number of trapezoids, i.e, it does not presume any relationship, that is

$$A \approx \sum_{j=0}^{n-1} \frac{f(x_{\mathrm{j}+1}) + f(x_{\mathrm{j}})}{2} \left| x_{\mathrm{j}+1} - x_{\mathrm{j}} \right| . \tag{8}$$

Technically speaking, by applying this method we assume that within an appropriately small Δx interval the real function can be approximated with a linear, that is, the area under the function equals to the area of a rectangular trapezoid. As a consequence of the measurements, the shear rate (γ) values are available as discrete entities. According to equation (8), the area of the trapezoids shown in the right panel of Fig. 6 is the half of that of the rectangle determined by the difference of the two shear rates ($x = \gamma / \mathrm{s}^{-1}$) and the sum of the two function values ($f(x) = \tau / \mathrm{Pa}$).

If you choose this method for data evaluation, add two extra columns (e.g., A_{ascend} and A_{descend}) to Table 3 to display the area corresponding for a given interval. If no shear stress can be measured for the investigated gel within a given shear rate interval, do not perform the evaluation on that interval. Be careful, due to the nature of the method, one less area can be calculated than the number of the measured points. After deriving the total area under the curves (e.g., $\sum A_{\mathrm{ascend}}$ and $\sum A_{\mathrm{descend}}$), calculate the area of the thixotropic loop as the difference of them.