University of Stavanger

FACULTY OF SCIENCE AND TECHNOLOGY

MASTER'S THESIS

Study programme/specialisation:	Spring/ Autumn semester, 2018
Petroleum Engineering:/ Reservoir Engineering	Open / Confidential

Author: Marina Lutskina	…………………………………………… (signature of author)

Programme coordinator:

Supervisor(s): Dmitry Shogin

Title of master's thesis:

Describing viscosity of IOR polymer solutions with
differential non-Newtonian fluid models

Credits: 30

Keywords: non-Newtonian viscosity, very dilute, Polymer flooding, differential models, FENE-P, PTT	Number of pages: ………………… + supplemental material/other: ………… Stavanger, …June/2018 date/year

Abstract

The non-Newtonian viscosity of multiple of polymers was measured.

For tests were taken polymers that are widely used in oil industry. They are: HEC; Xanthan gum; Polypack; Flopaam: 5115VHM, 5115VLM, AN 125VHM, AN 125VLM, 3610VHM, 3130S.

These polymers were dilute to a number of low concentrations and viscosity for all of them was measured at rheometer with a cone-plate tool. All calculated and measured values are recorded in tables and presented in Experimental section [2].

The graphical analysis was performed for each polymer and trends were identified and compared between different polymers. The regions with "very dilute" concentrations were identified. This helped to find a criterion for "very dilute" solution. Such knowledge is very important due to gives a key to understanding what model can be applied for this particular polymer at this particular concentration.

Then data from measurements were tested against the prediction curves of several advanced, physic-based non-Newtonian models. These models are Finitely Extensible Nonlinear Elastic-Peterlin (FENE-P) dumbbell model, which was designed for dilute concentrations and exponential Phan-Thien-Tanner model (PTT), which was designed for concentrated solutions.

The ranges of concentrations with a good correlation between data points and model curves were identified for each polymer. Results from different polymers were compared and some similarity in trends identified.

The section Conclusions [4] sum up all conclusions that were made after experiments and analysis of model prediction.

Acknowledgements

I would like to express my great appreciation to my supervisor, Dr. Dmitry Shogin for his support and guidance, as well as his tremendous enthusiasm and ability to work with students.

He opened a door for me into the unknown world of non-Newtonian liquids. Within a short period of time he delivered a comprehensive course in polymer fluid dynamics to us. During this course he has presented key features of polymer fluids, as well as main equations and models that describe their behaviour.

He gave us clear recommendations about laboratory work: what is the aim of our tests; how it should be interpreted, and how these results will be used. During our lab work Dmitry regularly visited our group to make sure that we felt comfortable doing experiments and to give advice where we experienced difficulties.

Dmitry also presented to us courses in LaTeX and Wolfram Mathematica. These are softwares similar to Word and Excel, but with better functionality and results presentation.

My great gratitude also goes to Kim Andre Vorland, who taught us how to use rheometers, mixers and magnet devices. In a very little time he has ordered missing equipment for our experiments and always was open for help.

I am also thankful to Jorunn Hamre Vralstad and Jostein Djuve for having enough patience and time to answer my questions regarding theory of lab work. I really appreciate their help in the lab, when I had difficulties with unexpected polymer behaviour.

And thank you to Mesfin A.Belaynech for maintaining such a positive mood in the lab, which helped keep up student spirits.

My thanks go also to my student colleagues involved in laboratory experiments, for their patience and ability to find compromise. Many thanks also go to my mum, who has encouraged and supported me in my studies, and did not let me give up.

Thank you for reading this.

Contents

List of Figures

List of Tables

Introduction

The Norwegian Petroleum Directorate has highlighted that the era of easy extraction of hydrocarbons has remained in the past, and the oil industry companies should focus on methodologies that help to improve oil recovery from the fields.

Polymer flooding is considered to be one of the most promising improved recovery methods, but it is not widely implemented on the Norwegian Continental Shelf because of lack of understanding of how polymer solutions behave. Therefore,it is so important to capture the fluid dynamics of polymers and the factors that change it. Developing advanced mathematical models of polymeric liquids based on microscopic physics is a cornerstone of this understanding.

This work is a part of a research program that focuses on the analysis of polymer behaviour and the identification of models that are best for predicting polymer behaviour in reservoirs with complex geometry. This document is divided into three main sections: Theory, Experiment and Analysis. Theoretical section gives an overview of the main rheology laws, as well as models that describe these laws mathematically to predict fluid behaviour. Since work is based on the analysis of polymers, here also presented a chapter Polymers, where described main polymer characteristics. Furthermore, main polymer characteristics are being outlined in a separate chapter to support the analysis of this work.

The experimental part of this document describes the experiments and the results of measurement. The viscosity, shear stress and shear rate were measured in rheometer. During the laboratory work all relevant equipment parameters, polymer concentrations, and some additional information about lab tests were recorded and presented in tables.

Graphs support a visual analysis of the obtained data. Several interesting zones with unexpected fluid behaviour were identified, and additional measurements were made in these regions. The graphs and their analysis is performed in a chapter Overview of laboratory data.

Afterwards, the laboratory results were used to test differential mathematical models. Comparison of real measurements and modelled ones is given in Section 3.

1   Theory

1.1   Polymers in oil industry

Recent statistic indicate that almost fifty percent of hydrocarbons remain in the reservoir after conventional production. Researches show that only a fraction of fields can be developed easily, while the majority call for more sophisticated development methods to sustain production. A popular Enhanced Oil Recovery technique is the injection of a special fluid to move the oil out of the reservoir [NPD 2018].

There is a variety of fluids that can be used for injection, each of which requiring its own methodology. The cheapest and simplest method is water flooding, where water is used to maintain pressure in the reservoir.
Further methods of enhanced oil recovery:

Gas injection; Heat injection; Chemical injection. Chemical injection using polymers or alkaline reagents.

Despite being a known technique and delivering good results, Polymer injection is not widely used mainly due to its high cost [NPD 2018].

Figure 1: Example of notuniform (a) and uniform (b) flow. Source:[Floerger 2015]

Better oil recovery can be achieved through increase of the microscopic sweep efficiency, as shown in Fig. 1. The upper picture a) visualizes the effect of water injection on an oil reservoir. It is clearly seen that for this case water does not form uniform flow, which can lead to quick water production. A uniform and good sweep efficiency is presented on picture b), when an injected fluid gradually replaces hydrocarbon. The more hydrocarbon is pushed out of grains and inner channels, the better the injected fluid is working. It should be noted, that the best suited injection fluid varies from field to field and from reservoir to reservoir, which is why the industry needs specialists to identify the appropriate fluids for each individual case. [Wever, Picchioni, and Broekhuis 2011]

The main job of a reservoir engineer is to study the reservoir: to identify forces acting inside and on the reservoir; to define hydrocarbon behaviour inside the reservoir and to predict its interaction with other fluids. It is very important to choose a right technique for improved hydrocarbon recovery to boost production, because wrong

method might even ruin the well or, at the very least, loss of resources and time [Jan, Cook, and Graham 2008].

Taking this into account the need for professionals to better understand fluid rheology becomes apparent. Furthermore, the knowledge of fluids with atypical behaviours, such as polymers, is crucial in order to predict their interactions with substances and model the forces acting inside. This is why this work is devoted to polymers and models that can predict their behaviour.

1.2 Polymers

What is a polymer?

In physics, any substance that has "macromolecules" is called a polymer. In this context macromolecule refers to a very long molecule. From chemical point of view, polymers are long molecules of repeated monomers. A monomer is a substance containing one or several units of identical molecules.

The word **polymer** is a combination of two Greek words: "poly" that means many and "meres" meaning parts. In chemistry such parts are called "units". Since monomers are highly reactive, they can join into long chains forming a polymer molecule [Zuev, Uspenskaya, and Olehanovich 2010].

A schematic formula transforming monomer to polymer is written:

$$\mathbf{nM} \rightarrow (\mathbf{-M-})_{\mathbf{n}}$$
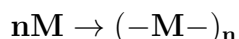
Polymers are widely present in daily life, both in nature and in synthetically created forms. They are not only seen in plastics, but also in shampoo, gels and glue, among other things. Even our body has its own polymers. DNA molecule, proteins and amino acids belong to the class of natural polymers.

Some natural polymers were known and used before the term polymer was applied to them. For instance, silk manufacturing from silkworms is well known in China since the antiquity. The length of thread from one silk cocoon can reach up to 1000 m, with its diameter measuring in micrometers. Similar tiny threads that have a natural origin can be observed in spider nests.

Another well-known natural polymer is rubber. James Prescott Joule studied the behaviour of materials under heat, and rubber was a subject of his close examination. He found that rubber under heating behaves like a gas. Joules experiments with rubber were the basis for the theory of high elasticity [Zuev, Uspenskaya, and Olehanovich 2010], [Bartenev and Frenkel 1990].

For a long time people were trying to make a substance that would have attributes similar to natural polymers, but it was not until the twentieth century that scientists finally managed to create a synthetic polymer. From this time onwards the "plastic boom" began. Polymers found their place in the cosmetic industry, decoration, dish manufacture, household equipment, construction, etc. Such a wide range of polymer applications led to the formation of a new field of science known as the "science of polymers".

Most synthetic polymers are polydisperse i.e. their molecules are not identical and have different length, as a consequence, different molecular weight. The average molecular weight can be calculated by formula 1 [R. B. Bird 1977].

$$\hat{M}_n = \frac{\sum_i N_i \, M_i}{\sum_i N_i} \tag{1}$$

There is a variety of ways to classify polymers, the main ones are:

1. spatial location of units:

   - Linear structure a large molecule is a chain of joined units, as shown in left Fig. 3;
   - Branched structure: a large molecule has additional branches; linked to the main chain, as shown in left Fig. 2;
   - Cross-linked structure a large molecule make links to each other, as shown in right Fig. 3;

2. origin

   - natural i. e. polymers that can be found in a nature;
   - artificial i. e. man-made polymers;

3. methods of their manufacture:

   - polymerization is a process of gradual addition of monomers into one large molecule;
   - polycondensation is a process where one group of molecules substitutes another group, during such reaction the gas/water liberation process takes place;
   - chemical modification is a process of change in structural or chemical composition of polymer under external impact [Teraoka 2002].
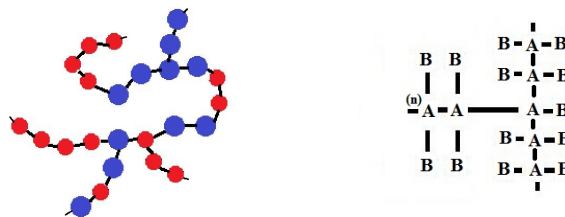
Figure 2:   Symbolic representations of branched macromolecule (left fig.) and a fragment of its structural unit (right fig.) Source:[R. B. Bird 1977]

Figure 3:   Symbolic representations of linear (left fig.) and cross linked molecule structure (right fig.)

1.3 Typical polymer behaviour

Several specific terms are used in this work which are defined in the following.

The word *fluid*, is very often used with the meaning *liquid*, not taking into account that gas is also fluid. Fluid a substance that does not have a constant shape and cannot resist stresses. Any shear force applied to it will cause the substanceto flow [**Batchelot1970**].

According to how they flow fluids can be divided into two major classes: Newtonian and non-Newtonian.

Fluids that behave like water and can be described by classical fluid dynamics laws are *Newtonian fluids*. Their mathematical description is relatively simple and can be fully characterised by two scalar properties - viscosity and density.

Viscosity is a property of fluids and solids to resist stress.
Non-Newtonian fluids are fluids that do not obey classical dynamic laws due to their composition: for example they can contain large molecules. To describe flows of such fluids more complex laws should be used.

An attempt to measure the viscosity of non-Newtonian fluids would reveal, that in the most cases, it depends on shear rate or pressure drop [R. B. Bird 1977]. A more detailed description of the characteristics of Newtonian and non-Newtonian fluids is given in Section 1.4.3.

The literature overview identified that majority of articles refers to the fundamental work of B. Byron Bird "Dynamics of polymeric liquids" , that is most valuable source of information up to date.

Most known polymer flow effects are described in the following, in general they can be divided in three groups:

1. "Variable" (shear/dependent)viscosity

   The classical experiment to show **shear-thining effect** is using two identical pipes, as it shown in Fig.4. One of pipes is filled with Newtonian and another with non-Newtonian fluid (for example: polymer). This experiment should be carried out when fluids have equal initial viscosity. To check that viscosities are equal we can use two small steel balls that fall inside the tested fluids. If the balls fall at the same speed, then fluids have equal viscosity. At the beginning of the experiment both pipes are fixed vertically and closed off at the bottom side, then pipes are simultaneously opened for the fluid to run out [R. B. Bird 1977].
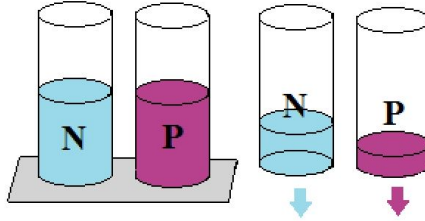
Figure 4: Beakers with Newtonian fluid (N) and polymer (P)

Non-Newtonian fluid flow faster than Newtonian, due to dependency between viscosity and shear rate. A decrease in viscosity with increasing shear rate is called shear-thinning, while the opposite is referred to as shear-thickening. Shear-thickening is a quite rare behaviour, most of non-Newtonian fluids show a shear-thinning dependence.

2. Normal stresses.

   A number of experiments can be explained by one additional force that occurs in non-Newtonian fluids (experiment with two plates; rod climbing; bubble squeezing). Analysing the behaviour of polymeric fluids Weissenberg put up the idea that under action of flow an extra tension arises along the streamlines, resulting in extra forces acting in the perpendicular direction. These forces are called *normal* [Weissenberg 1947].

   One experiment that can be explained by this hypothesis is a setup of with two plates with polymer between them. The upper plate is moving in horizontal direction inducing straight stream lines and a normal force acting perpendicular to stream lines. This causes the upper plate to be pushed upwards.

   Rod climbing, also known as the Weissenberg effect is the feature of a polymer solution to climb a rod under mixing.

   A classic experiment to show the Rod climbing effect contains a beaker with a Newtonian fluid and another beaker with a polymer solution. A mixer is inserted into both fluids and set in motion causing the Newtonian fluid to form a crater, while the polymer wraps around the rod. Increasing rotation speed leads to an increased amount of fluid climbing onto the rod, as shown in Fig. 5

   This effect cannot be explained by shear dependent viscosity. It originates from the ratio between normal and centrifugal forces. Upon rotation of the rod, the stream lines form circles around the centre. This produces normal forces directed radially inwards and centrifugal forces acting radially outwards . If normal forces are larger than centrifugal forces, then the polymer will be pushed upwards and climb the rod. An example of rode climbing from lab

tests can be seen in Fig. 6. In Newtonian fluids, no normal forces are present; centrifugal forces move the fluid towards the walls of the beaker.
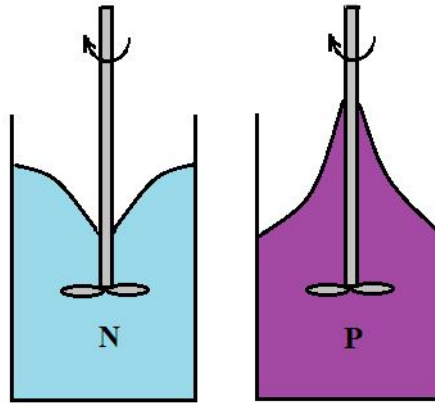
Figure 5:   Example with Newtonian and non-Newtonian fluid under mixer rotation
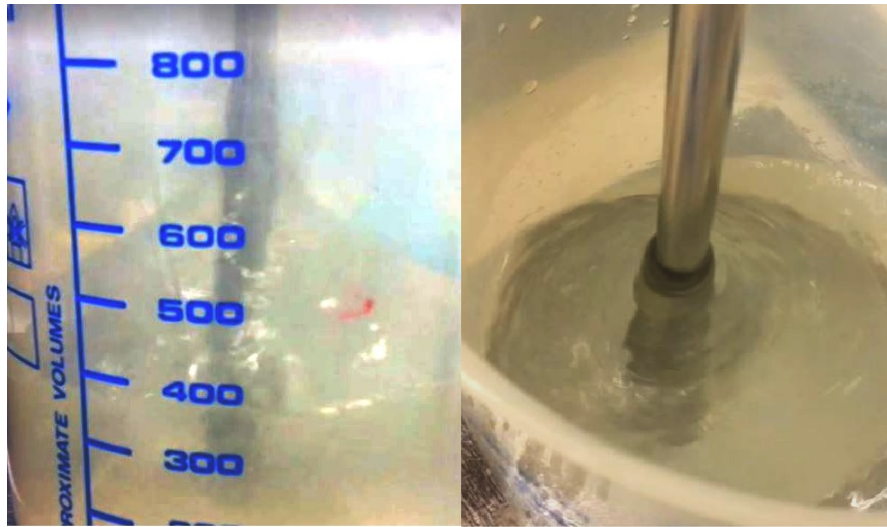
Figure 6:   Lab photos with polymer at mixer rotation

Such behaviour can be seen even without a rod: two beakers are set up, one with water, another with a polymer. A magnet is added into both beakers and they are placed on a magnetic stirrer. When the magnet inside the beaker starts to rotate and generates a flow, the polymer moves upwards and the surface of fluid became convex. The higher speed of magnet rotation, the higher will be

the normal forces and the clearer the effect, as shown in right Fig.7. The same experiment with the water in a beaker will form a typical vortex, as shown in left Fig. 7.

Figure 7:   The beaker with magnet inside is set into magnet field. (left fig.) beaker with polymer (right fig.) beaker with water

Another example of normal stress action can be seen in a flow of polymer containing bubbles.The flow is stretching the molecules along stream lines, while intramolecular forces are trying to compress the molecules. Since the bubble is between stream lines it undergoes normal forces directed perpendicular to the stream lines and, as a result, the bubble is squeezed, as shown in Fig. 8
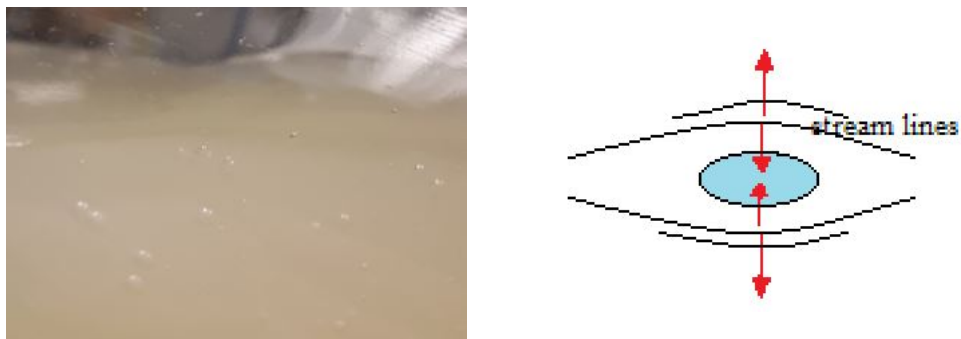
Figure 8:   Bubbles in a rotated polymer fluid (left fig.) lab photo (right fig.) schematic force action

Swelling effect, also called fading memory.

The classic experiment to show the swelling effect is an experiment with a polymer being extruded from a pipette. The non-Newtonian fluid jet, right after it came out from a pipette neck, will increase in diameter, as shown in left Fig. 9 This can be explained by normal stress. The flow is directed downwards stretching the polymer molecule along vertical stream lines. The "extra tension" along the stream lines (elastic forces) makes the fluid flow down slower, and the normal forces cause the jet to expand radially. In a right Fig. 9 the Normal forces are drawn in a red colour, elastic forces in magenta. [R. B. Bird 1977]
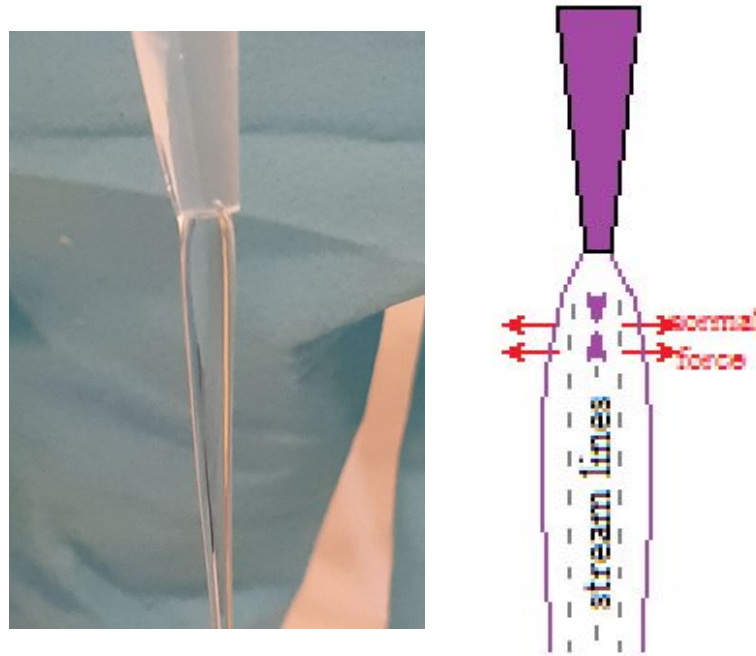
Figure 9:   Polymer in pipette. (left) lab photo (right) schematic force action

As it can be seen from the rod-climbing experiment, the normal forces are very important, because they can affect the flow pattern dramatically. They can be measured, for example, using a *cone and plate* in rheometer; where a tested fluid is placed between two plates and the upper plate is rotated. The equipment measures both normal and shear forces that act on plates and then calculates viscosity and other rheological parameters from them (more detailed info is given in the Experimental part, section 2.4).

3. "Memory" effects

   Elastic recoil: This effect shows that polymer aim to turn back to the condition before the stress was applied. This experiment is widely used for demonstration of polymer behaviour in the class rooms, due to its demonstrative effect, however this experiment does not allow to measure any property.

   In classic way, this experiment should be carried out with aluminium soap solution that is poured out of a beaker and then cut into parts. After that, the upper part will rebound to the top, while the lower part will fall. The same fluid behaviour was observed during our laboratory work with polymers, it shown in Fig.10 When the polymer solution was poured out from one beaker to another. Then at a certain moment pouring is stopped, and the beaker is kept inclined, and stream was cut the upper part of stream rebound to the upper beaker and lower part fall down. [R. B. Bird 1977]

a)   b)
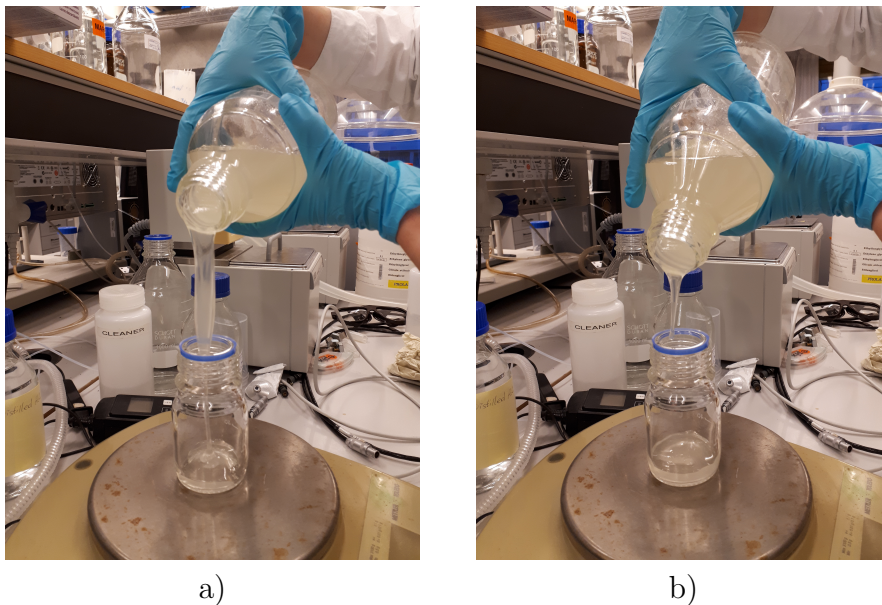
Figure 10: Polymer at pouring a) and polymer when pouring stopped

These phenomena all have the same origin "hidden" in the microscopic nature of polymeric fluids. Mathematical description of such behaviour cannot be done using models based on Newtonian fluid behaviour and must be formulated in terms of tensors.

Introduction to mathematical description

This mathematical section starts with equations of fluid dynamics, also called the "Navier-Stokes" equations. They are differential equations in partial derivatives. The elements of these equations are scalars, vectors and tensors.

A scalar is a quantity that can be fully described by one number. Temperature, time, mass are examples of scalar physical quantities.

A vector is a mathematical object associating a number to each direction. for example: force, velocity, acceleration are vector quantities and have a component in each of the three directions.

A tensor (of rank 2) associates a number to each ordered pair of directions. There are a lot of such quantities in physics, in particular when it comes to describing deformations and forces acting inside a medium. Tensors transform from one coordinate system to another in according to specific laws, presented in [V.U.Topolov 2002].

To distinguish between these quantities we accepting following notation:

- or scalars normal Latin font will be used

- for vectors boldface Latin font will be used

- tensors will be written using boldface Greek font

also, we use different brackets:

$()$ the quantity inside round brackets is a scalar

$[]$ the quantity inside square brackets is a vector

$\{\}$ the quantity inside curly brackets is a tensor

The cube with vectors is presented in Fig. (**fig tensor cube**)

1.4   Equations of fluid dynamics (Generalized Navier-Stokes)

For many engineering applications it is necessary to understand flow pattern. Velocity and forces acting in a flow are the main quantities of interest. Equations of fluid dynamics define the motion of any fluid.

Equations of fluid dynamics are mathematical representation of three fundamental physical laws :
- conservation of mass,(the continuity equation of fluid flow)
- conservation of momentum, (the momentum equations of fluid flow)
- conservation of energy, (the energy equation)

These equations are applied in: aircraft and vehicle manufacturing, buildings and bridges construction and anywhere, when it is important to understand flow behaviourAnderson 1995].

For derivation of these equations an arbitrary fixed volume in a flow field should be introduced. This finite volume is called "control volume" in Fig. 11 [R. B. Bird 1977].
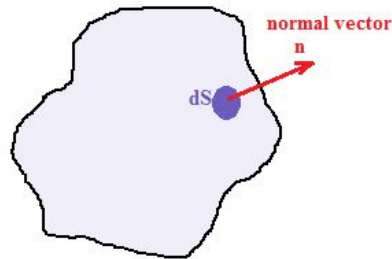
Figure 11: Control volume, with a normal vector

Where:

V - volume;
S - area of the surface surrounding V;
$\mathrm{d}S$ - infinitesimal surface element;
$\mathbf{n}$- a unit vector, normal to the surface at any point;
$\mathbf{v}$ - velocity of the fluid.

1.4.1 Conservation of mass

Law of conservation of mass state: The total mass of the fluid inside volume V will increase only due to the flow of fluid across the boundary S [R. B. Bird 1977]. Then one can write:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho \mathrm{d}V = -\int_S (\mathbf{n} \cdot \rho\mathbf{v})\ \mathrm{d}S \tag{2}$$

where:

The left hand side shows a total rate of increase of mass inside the V The right hand side expresses the total mass flow rate of the fluid into V Applying the Gauss theorem, one gets:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho \mathrm{d}V = -\int_V (\boldsymbol{\nabla} \cdot \rho\mathbf{v})\ \mathrm{d}V \tag{3}$$

Since there are two volume integrals, they can be moved onto one side and the derivative can be placed inside the integral, creating an equation with a single integral over volume. Mathematical rules state that if an integral of function at any interval is equal to zero then the function under the integral is also equal to zero and the final equation takes form:

$$\frac{\partial \rho}{\partial t} = -\left(\boldsymbol{\nabla} \cdot \rho \mathbf{v}\right) \tag{4}$$

For incompressible liquids $\rho = 0$, this reduces to $(\boldsymbol{\nabla} \cdot \mathbf{v}) = 0$

1.4.2   Conservation of momentum

The law of momentum conservation states: "The total momentum of the fluid within volume V will increase because of a net influx of momentum across the bounding surface and because of the external force of gravity acting on the fluid." Here net influx is presented by bulk flow and by molecular motions. In other words, there is a contribution from macroscopic (bulk flow) and microscopic (molecular) motion to molecular transfer[R. B. Bird 1977].

One can write:

$$\frac{\mathrm{d}}{\mathrm{d}t} \int\limits_V \rho \mathbf{v} \mathrm{d}V = -\int\limits_S [\mathbf{n} \cdot \rho \mathbf{v}\mathbf{v}] \, \mathrm{d}S - \int\limits_S [\mathbf{n} \cdot \boldsymbol{\pi}] \mathrm{d}S + \int\limits_V \rho \, \mathbf{g} \mathrm{d}V \tag{5}$$

Where:

Left hand side: rate of increase of fluid momentum inside$V$

Right hand side: contributions from fluid flow, microscopic processes, and external forces, respectively.

$\boldsymbol{\pi}$ is called the total stress tensor of the fluid and has the following physical sense:

π_{ij} is the rate of transfer of j momentum through a surface perpendicular to "j" direction.

Alternatively π_{ij} can be interpreted as the force per unit area acting in "j" direction onto a surface perpendicular to "i" direction.

After applying Gauss theorem one can get:

$$\int\limits_V \frac{\partial}{\partial t} \rho \mathbf{v} \mathrm{d}V = -\int\limits_V [\boldsymbol{\nabla} \cdot \rho \mathbf{v}\mathbf{v}] \, \mathrm{d}V - \int\limits_V [\boldsymbol{\nabla} \cdot \boldsymbol{\pi}] \mathrm{d}V + \int\limits_V \rho \mathbf{g} \mathrm{d}V \tag{6}$$

since integrals in a formula are taken for the same volume they can be taken under one integral sign, and formula can be rearranged in a way:

$$\int\limits_V \left(\frac{\partial}{\partial t} \rho \, \mathbf{v} + \boldsymbol{\nabla} \cdot \rho \mathbf{v}\mathbf{v} + \boldsymbol{\nabla} \cdot \boldsymbol{\pi} - \rho \mathbf{g} \right) \mathrm{d}V = 0 \tag{7}$$
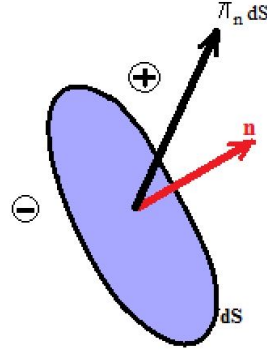
Figure 12: Force π on element dS

and since integral is equal to zero, and the volume is arbitrary, then the function under integral is zero, and equation can be rewritten as [R. B. Bird 1977] :

$$\frac{\partial}{\partial t}\rho\mathbf{v} = -[\boldsymbol{\nabla} \cdot \rho\mathbf{v}\mathbf{v}] - [\boldsymbol{\nabla}\boldsymbol{\pi}] + \rho\mathbf{g} \tag{8}$$

1.4.3   Stress tensor

It is convenient to decompose $\boldsymbol{\pi}$ according to:

$$\boldsymbol{\pi} = P\boldsymbol{\delta} + \boldsymbol{\tau} \tag{9}$$

where
$\boldsymbol{\tau}$ the anisotropic stress tensor.
At equilibrium (no flow) $\boldsymbol{\tau}$=0
P the thermodynamic pressure.
For the description of forces acting on a body it is convenient to consider a vector cube Fig.13. It shows planes on which forces are acting and in what direction forces are acting.

There are three different vectors, each defining one plane and being perpendicular to the plane σ. They have identical symmetrical vectors that directed in opposite direction, these vectors called *stress*. There are two different vectors that are acting within one plane τ. Such forces are called *shear stress*. Considering cube symmetry there are 6 different shear stresses, and each of them has the one identical vector in the opposite direction [Shaw 2012] and [R. B. Bird 1977].

Mathematically, all forces that are acting in a cube can be written in a general form of stress tensor, which can be applied for any object:
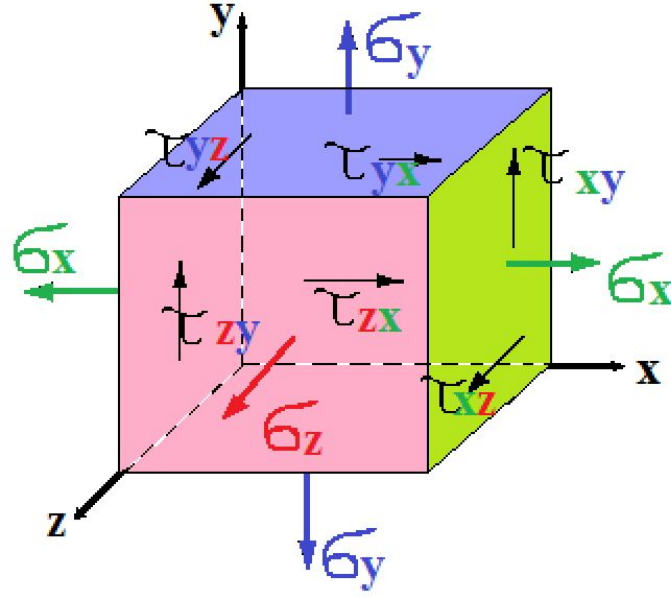
Figure 13: 3D stress tensor

$$
\begin{bmatrix}
\tau_{xx} & \tau_{xy} & \tau_{xz} \\
\tau_{yx} & \tau_{yy} & \tau_{yz} \\
\tau_{zx} & \tau_{zy} & \tau_{zz}
\end{bmatrix}
=
\begin{bmatrix}
\sigma_{xx} & \tau_{xy} & \tau_{xz} \\
\tau_{yx} & \sigma_{yy} & \tau_{yz} \\
\tau_{zx} & \tau_{zy} & \sigma_{zz}
\end{bmatrix}
\tag{10}
$$

where:

diagonal components - *normal stress*

off-diagonal components - *shear stress*

In a simple shear flow Newtonian fluid does not have normal stresses, from the Fig. 13 is seen that stress tensor has six shear and three normal components and components of normal stress are equal to zero .[Shaw 2012] and [R. B. Bird 1977]

An equation specifying τ is called a constitutive equation of the fluid. Newton argumented that if the fluid flows with velocity which is the same in all points in space, that would not produce any stresses. He stated then that τ must depend not on **V** but on its derivatives, and assumed this dependency is linear.

The most general form that corresponds to this Newton's hypothesis is equation 11, this was proved experimentally for fluids with small molecules, which we call *Newtonian fluids*:

$$
\boldsymbol{\tau} = -\mu \left\{ (\boldsymbol{\nabla}\mathbf{v}) + (\boldsymbol{\nabla}\mathbf{v})^T \right\} + \left(\frac{2}{3}\mu - \kappa \right) (\boldsymbol{\nabla} \cdot \mathbf{v})\,\boldsymbol{\delta}
\tag{11}
$$

where:
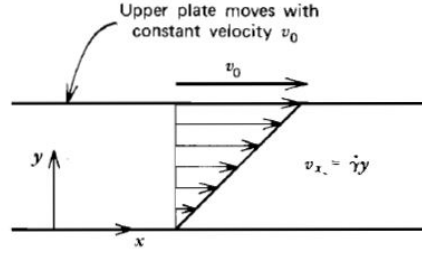
Figure 14: Steady simple shear flow between parallel plates [R. B. Bird 1977]

μ is the coefficient of viscosity and κ is the bulk viscosity which appears for compressible flows;

For incompressible liquids $(\boldsymbol{\nabla} \cdot \mathbf{v}) = 0$ and

$$\boldsymbol{\tau} = -\mu \left\{ (\boldsymbol{\nabla}\mathbf{v}) + (\boldsymbol{\nabla}\mathbf{v})^{T} \right\} = -\mu\dot{\boldsymbol{\gamma}} \tag{12}$$

$\dot{\boldsymbol{\gamma}}$ is called rate-of-strain tensor.

It follows from this equation that stress tensor is fully determined by only one constant μ which is a "material constant". From Equation(12) one can see that when there is no flow, $\dot{\boldsymbol{\gamma}} = 0$, indeed, $\boldsymbol{\tau} = 0$, as expected.

For non-Newtonian fluids Eguation(11) does not work. The flow behaviour of non-Newtonian fluids is more complex than for Newtonian. It can be characterized by so-called material functions. Different material functions are introduces for different flow types [D.Shogin 20018].

1.4.4   Flow types

As mentioned above, the stress tensor varies depending on the type of flow. There are many different types of fluid flow, and most of them are complex flows. In the following , shear and shearfree flow; steady and unsteady flow will be described.

Steady flow is a flow with parameters independent of time, in the sense that the parameters for each location in the flow will be constant in time.

The most common way to describe shear flow is to use flow between two parallel plates as a simple example. A precise mathematical definition of shear flow can be found in [R. B. Bird 1977]. To produce a shear flow the upper plate is moved with constant velocity, resulting in an identical velocity gradient in different parts of flow, as shown in Fig. 14

The flow between two parallel plates can be considered as a flow of equal shearing surfaces with equal gap between them. These surfaces are parallel to the bounding plates, and these surfaces move with constant velocity. Velocities in each layer are different. [R. B. Bird 1977]

For this flow, the velocity profile is linear and described by:

$$v_x = \dot{\gamma}_{yx}\, y$$
$$v_y = 0$$
$$v_z = 0$$

The rate of strain tensor $\dot{\boldsymbol{\gamma}}$ has only one independent non-zero component, namely $\dot{\gamma}_{xy}$; its absolute value is called the local shear rate;

shear rate tensor:

$$\dot{\boldsymbol{\gamma}} = \begin{bmatrix} 0 & \dot{\gamma}_{xy} & 0 \\ \dot{\gamma}_{xy} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \dot{\gamma} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{13}$$

For a general fluid the stress tensor for simple shear flow takes the form [R. B. Bird 1977]:

$$\pi = p\delta + \tau = \begin{bmatrix} p + \tau_{xx} & \tau_{yx} & 0 \\ \tau_{yx} & p + \tau_{yy} & 0 \\ 0 & 0 & p + \tau_{zz} \end{bmatrix} \tag{14}$$

Thus simple shear flow can be described by:

τ_{yx} shear stress
$\tau_{xx} - \tau_{yy}$ first normal stress difference (FNSD)
$\tau_{yy} - \tau_{zz}$ second normal stress difference) (SNSD)

The material functions for a steady simple shear flow are functions of shear rate and are introduced by[R. B. Bird 1977]:

$$\tau_{xx} - \tau_{yy} = -\Psi_1\left(\dot{\gamma}\right)\dot{\gamma}_{yx}^2 \qquad \Psi_1 \qquad \text{first normal stress coeficient}$$
$$\tau_{yy} - \tau_{zz} = -\Psi_2\left(\dot{\gamma}\right)\dot{\gamma}_{yx}^2 \qquad \Psi_2 \qquad \text{second normal stress coeficient}$$
$$\tau_{yx} = -\eta(\dot{\gamma})\dot{\gamma}_{yx} \qquad \eta \qquad \text{is non-Newtonian viscosity}$$

For Newtonian fluids $\eta(\dot{\gamma}) = \mu$ and independent of $\dot{\gamma}$.

The normal stresses are absent $\Psi_1 = \Psi_2 = 0$.

Power law region The most common way to analyse experimental data is by making a plot. To study shear flow it is convenient to investigate how viscosity changes with shear rate. It is common, to use a logarithmic scale, because at linear scale it is difficult to identify power-law region, while on log-log scale power-law will be presented as a straight line, as it shown in Fig. 15 There are 3 regions on a curve: at very low shear rates the viscosity is almost constant and approaches zero value η_0, this viscosity is called the " zero-shear-rate viscosity" and the region where shear rate is very small is called a " Lower Newtonian region".

At very high shear rates the viscosity approaches another constant value which is called the "infinite shear rate viscosity" η_∞ and region is called "Upper Newtonian region" For majority of non-Newtonian fluids, including polymers and polymer solutions $\eta_\infty < \eta_0$, and viscosity monotonically decreases as a function of shear rate and which is called "shear thinning" behaviour. For polymer melts experiments have shown that η_∞ is the viscosity of the solvent [R. B. Bird 1977].
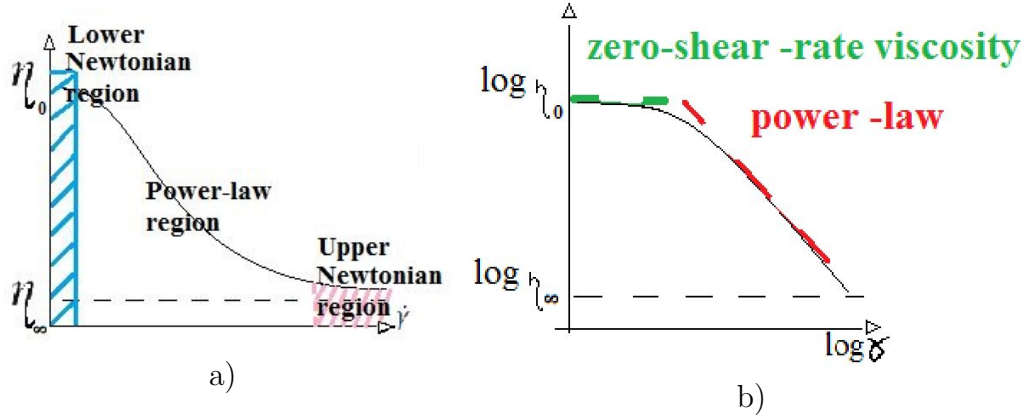
Figure 15: Power-law region. a) linear scale with polymer b) log-log scale

Shearfree flow

"A shearfree flow is defined as a flow for which it is possible to select for every fluid element an orthogonal set of unit vectors fixed in the element so that referred to these axes the rate-of-strain tensor has a diagonal form:" [R. B. Bird 1977]

$$\dot\gamma = \begin{bmatrix} \dot\gamma_{11} & 0 & 0 \\ 0 & \dot\gamma_{22} & 0 \\ 0 & 0 & \dot\gamma_{33} \end{bmatrix} \tag{15}$$

It can be seen from this matrix that shearfree flow is a flow in which the rate-of-strain tensor has only main diagonal components. The volume in the flow considered constant: $\dot\gamma_{11} + \dot\gamma_{22} + \dot\gamma_{33} = 0$
in terms of velocities shearfree flow is described by:

$$v_x = -\frac{1}{2}\dot\epsilon(1+b)x \tag{16}$$

$$v_y = -\frac{1}{2}\dot\epsilon(1-b)y \tag{17}$$

$$v_z = +\dot\epsilon\, z \tag{18}$$

Shearfree flow includes three types of flow and parameter b distinguish exact type:
    parameter $\dot\epsilon$ is elongational rate (can be dependent on time)
        biaxial stretching flow: $b = 0; \dot\epsilon < 0$
        elongational flow: $b = 0\,; \dot\epsilon > 0$
        planar elongational flow: $b = 1$

19

Elongational flow can be considered as a flow between two plates with polymeric fluid between them, and if plates move close to each other then polymer will be squeezed and running out of plates; if distance between plates will be increased, then fluid will try minimize itself and stay inside a gap.

The shear stress tensor for shearfree flow takes form:

$$\boldsymbol{\pi} = p\boldsymbol{\delta} + \boldsymbol{\tau} = \begin{bmatrix} p + \tau_{xx} & 0 & 0 \\ 0 & p + \tau_{yy} & 0 \\ 0 & 0 & p + \tau_{zz} \end{bmatrix} \tag{19}$$

the flow can be determined by:

$$\begin{aligned} \tau_{zz} - \tau_{xx} & \quad \text{first normal stress difference (FNSD)} \\ \tau_{yy} - \tau_{xx} & \quad \text{second normal stress difference (SNSD)} \end{aligned} \tag{20}$$

for flows with $b = 0$ second normal stress difference will be zero $(\tau_{xx} - \tau_{yy}) = 0$, so to describe such flows as *elongational* and *biaxial stretching* it is enough to know only the first normal stress difference.

Equations for **material functions** in elongational flow [R. B. Bird 1977]:

$$\tau_{zz} - \tau_{xx} = -\hat{\eta}_1 (\dot{\epsilon}, b) \dot{\epsilon}$$
$$\tau_{yy} - \tau_{xx} = -\hat{\eta}_2 (\dot{\epsilon}, b) \dot{\epsilon}$$

For the steady-state shearfree flow, with $b = 0$,

$\hat{\eta} = \hat{\eta}_1(\dot{\epsilon})$ $\hat{\eta}_2(\dot{\epsilon}) = 0$ $\hat{\eta}$ is called the elongational or Trouton viscosity. For polymers it shows a complex behaviour R. B. Bird 1977, but generally increases with elongation rate. This is called "elongational thickening". For Newtonian fluids $\hat{\eta} = 3\mu$ and is independent of $\dot{\epsilon}$

Unsteady shear flow

There is a group of flows that are combined under this name, but we consider only the small-amplitude oscillatory flow.

This flow is varied in time. To describe fluid behaviour, as well as in previous cases, consider a flow between two parallel plates where upper plate is oscillating with frequency ω, as it shown in Fig. 17 and this oscillation must have very small amplitude. Under such action a fluid between plates will exhibit variable behaviour in response to oscillation [R. B. Bird 1977].

Schematically, fluid response to oscillation and dependence of stresses on time can be presented by sinusoidal curves:

Curves of shear rate and shear stress for Newtonian fluid go in one phase, whereas curves of shear rate and shear stress for non-Newtonian fluids go with different phases, they are sifted with respect to each other. While Newtonian fluids have no normal stress differences, this is not true for non-Newtonian fluids.Experiments show that the FNSD oscillates around a non-zero average with frequency 2ω. The same holds for the
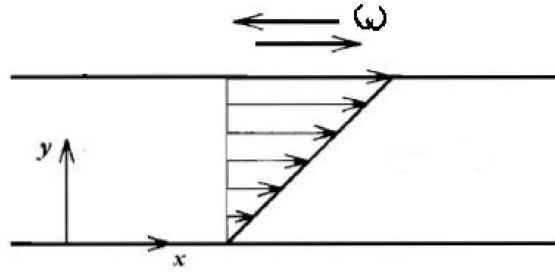
Figure 16: Flow with oscillation upper plate R. B. Bird 1977
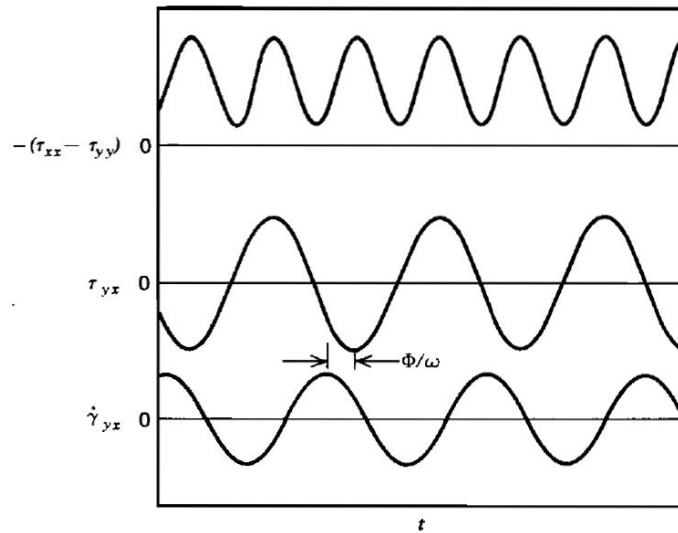
Figure 17:   Oscillating shear rate, shear stress, and First normal stress difference [R. B. Bird 1977]

SNSD [R. B. Bird 1977]. The oscillatory flow material functions can be introduced by:

$$\tau_{yx} = -\eta'(\omega)\dot{\gamma}^0_{yx}\cos\omega t - \eta''(\omega)\dot{\gamma}^0_{yx}\sin\omega t \tag{21}$$

$$\frac{(\tau_{xx} - \tau_{yy})}{(\dot{\gamma}^0_{yx})^2} = -\Psi^d_1(\omega) - \Psi'_1(\omega)\cos 2\omega t - \Psi''_1(\omega)\sin 2\omega t \tag{22}$$

$$\frac{(\tau_{yy} - \tau_{zz})}{(\dot{\gamma}^0_{yx})^2} = -\Psi^d_2(\omega) - \Psi'_2(\omega)\cos 2\omega t - \Psi''_2(\omega)\sin 2\omega t \tag{23}$$

Where:

$\eta'(\omega)$, $\eta''(\omega)$ components of the complex viscosity;

Ψ^d_1 and Ψ^d_2 first and second normal stress displacement coefficients stress coefficients;

Ψ'_1, Ψ'_2, Ψ''_1, Ψ''_2 components of complex first and second normal stress coefficients

   For Newtonian fluids: $\eta'(\omega) = 0$, i.e. independent on ω.

In summary to this section, there are many material functions and it is not possible to use correlations for all of them.

In simple flows, it is easy to isolate some specific effects and to identify correlations.

In a complex flow however, it is not possible to split these effects, and simple correlations do not apply here. To describe such flows, advanced non-Newtonian fluid models are needed. Such models are based on fundamental physics; the material functions are predicted from the constitutive equations and can be used to calibrate the models to experiments.

1.5 Generalized Newtonian models

With the aim of simplifying calculations "Generalized Newtonian" models were introduced. It is only assumed viscosity depends on the shear rate. The equation is similar to Newtonian constitutive equations, with an important note, that viscosity is a function dependent on components of stress tensor

$$\boldsymbol{\tau} = -(\eta\,\dot\gamma)\dot{\boldsymbol{\gamma}}$$

Even though "Generalized Newtonian" models are widely used for calculations it is important to keep in mind that it does not describe fluid behaviour at complex geometry. This class of models works only for steady shear flow.

All models are developed with aim to predict a linear region between two plateaus, i.e. power-law region on a plot viscosity vs shear rate.

1.5.1 Power-Law model

is the simplest and most used model.

Ostwald and Waele, based on experimental data proposed a formula:

$$\eta(\dot\gamma) = m\,\dot\gamma^{n-1}$$

where:

$$
\begin{array}{ll}
\eta(\dot\gamma) & \text{apparent viscosity;} \\
k & \text{constant that called "consistency constant";} \\
n & \text{power-law index;} \\
\text{when } n > 1 & \text{shear thickening;} \\
n < 1 & \text{shear thinning;}
\end{array}
$$

In a practice, the Lower-Newtonian region is very small and only for flow at high shear rates it is convenient to use this model.

Disadvantage of this model that it does not describe viscosity at low shear rates and it have limitations inherent to the class of Generalized Newtonian models i.e. works only in a simple shear flow [B. B. Bird, Curtiss, and Armstrong 1987].

1.5.2 Carreau Yasuda

is most detail model in this class. Main focus of this model to fit theoretical viscosity curve to real data. Carreau and Yasuda have modified a power-law model to get upper and lower boundary that is determined experimentally in relation viscosity vs shear rate.

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = [1 + (\lambda\,\dot\gamma)^2)]^{(n-1)/2} \tag{24}$$

where:

$$
\begin{array}{ll}
\eta_0 & \text{zero shear rate viscosity} \\
\eta_\infty & \text{infinite shear rate viscosity} \\
\lambda & \text{time constant, sets the "onset" of shear thinning}
\end{array}
$$

n   power-law index

the physical meaning of n is a slope that represents a power-law region

Even though that this model is more universal, it again has all limitations essential for the class of Generalized Newtonian models.[B. B. Bird, Curtiss, and Armstrong 1987]

1.6   Physical non-Newtonian fluid models

All efforts to build a model that can predict flow behaviour based only on mathematical derivations are failed, even the most complex model (Oldroyd-B), that has tensor equations does not describe real properties like shear thinning, elongational flow etc. It means, that using only math is not enough to build a model with good prediction, we should include physical meaning in mathematical equations.

1.6.1   Hookean dumbbells

Since this class of models is focused on non-Newtonan fluids, namely on polymers, then real polymer properties should be included in model. Most representative property is orientability and stretchability i.e ability to align along the flow, to change shape of molecule (coil or stretching)

This is a simple model that describes a polymer molecule like two beads connected by spring, as shown in Fig. 18. In Hookean model the force between beads assumed to be linear, Equation (25)

Figure 18:   polymer molecule in Hookean dumbbell model

$$\mathbf{F} = H\mathbf{Q} \tag{25}$$

where: F spring force

H spring stiffness

It is relatively easy to derive constitutive equations for dilute solutions in Hookean model by means of kinetic theory [B. B. Bird, Curtiss, and Armstrong 1987]. It turns out, however, that this model is too simple; it does not describe shear thinning and elongational viscosity is approaching infinity at finite elongational rates.

This model does not take into account non-linearity and finite extensibility of real molecules. The next model includes these properties.

1.6.2   FENE Dumbbell

Finitely Elongated Nonlinear Elastic model

Warner has proposed to consider non-linear elastic spring, which can expand only up to some maximum. In other words the connector force in this model is linear at very small extensions and is limited at high extensions.

$$\mathbf{F} = \frac{H\,\mathbf{Q}}{1 - (\frac{Q}{Q_0})^2} \tag{26}$$

where: F spring force
H spring stiffness
$\mathbf{Q}$ vector between beads
Q spring length
Q_0 max spring length
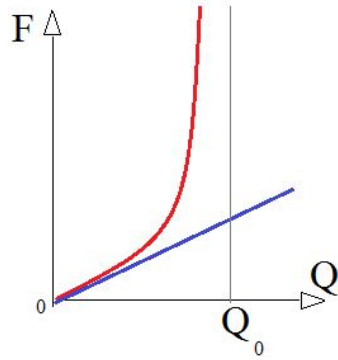
Figure 19:   relation between force (F) and spring length (Q) for FENE (red) Hookean(blue) dumbbell model

This figure shows that for FENE model, force is increasing very fast and spring can be expanded only up to length Q_0

For this model it is not possible to derive constitutive equations without making additional assumptions [B. B. Bird, Curtiss, and Armstrong 1987].

1.6.3   FENE-P Dumbbell

Peterlin has proposed to replace the average of the elastic force by mean-squared value. Such pre-averiging assumption is known as Peterlin closure. The model got a letter P as a honour to Pterlin "FENE-P" [V. Heel 2000]

The full constitutive equation for FENE-P:

$$\boldsymbol{\tau} = \boldsymbol{\tau_s} + \boldsymbol{\tau_p} \tag{27}$$

where: $\boldsymbol{\tau_s}$ is solvent contribution and $\boldsymbol{\tau_p}$ is polymer contribution
we assume that solvent is Newtonian [Shogin, Amundsen, and Hiorth 2017]:

$$\boldsymbol{\tau_s} = -\boldsymbol{\mu_s}\dot{\boldsymbol{\gamma}} \tag{28}$$

Regarding the polymer contribution the following constitutive equation is derived:

$$Z\boldsymbol{\tau}_p + \frac{C_3}{2}\boldsymbol{\tau}_{p(1)} - \left(\frac{C_3}{2}\tau_p - \delta\right)\frac{\mathrm{D}\,lnZ}{\mathrm{D}t} = -\dot{\gamma} \tag{29}$$

$$Z = C_1 - \frac{2C_2}{C_3}\mathrm{tr}\left(\tau_p\right) \tag{30}$$

where: C_1, C_2, C_3 are parameters of the model, they are constant and different for each polymer.

Assumptions taken for this model: we deal with polymer solution and it should be dilute solution.

This model can predict all mentioned non-Newtonian flow phenomena, i.e it gives a good qualitative prediction. Known weakens it gives too large deviation from experiments in time dependent flows. [A. P. G. v. Heel, Hulsen, and Brule 1997]

1.6.4   FENE-P Bead-Spring-Chain

This model is an expanded version of FENE-P dumbbells, it considers polymer molecules as chains of beads connected by elastic FENE springs.

Figure 20:   polmer molecule in FENE-P chain model

The assumption taken In this model is that beads and springs are identical. The model has an additional parameter N:

N is a number of beads,

N-1 is number of springs.

We can expect that with increase in N, the molecular weight will increase.
Equations describing this model [R. B. Bird 1977]:

$$\boldsymbol{\tau} = \sum_{n=1}^{N-1} \tau_j \tag{31}$$

$$Z_j\boldsymbol{\tau}_j + \lambda_j\boldsymbol{\tau}_{j(1)} - (\boldsymbol{\tau}_j - nkT\boldsymbol{\delta})\lambda_j\frac{\mathrm{D}\,lnZ_j}{\mathrm{D}Z} = -\,nkT\lambda_j\dot{\gamma} \tag{32}$$

$$Z_j = 1 - \frac{3}{b}\left(1 - \frac{tr\tau_j}{3nkT}\right) \tag{33}$$

It can be reformulated in terms of constants:

$$Z_j \boldsymbol{\tau}_p^{(j)} + \frac{C_3^{(j)}}{2} \boldsymbol{\tau}_{p(1)}^{(j)} - \left(\frac{C_3}{2} \tau_{p(j)} - \delta \right) \frac{D \ln Z_j}{Dt} = -\dot{\gamma} \tag{34}$$

$$Z_j = C_1^{(j)} - \frac{2C_2^{(j)}}{C_3^{(j)}} \operatorname{tr} \tau_p^{(j)} \tag{35}$$

The time constants λ are not independent. They are given by:

$$\lambda_j = \lambda \cdot 2c_j c_j = \frac{1}{4 \sin^2(j\pi/2N)} \tag{36}$$

Overall, the model is similar to FENE-P dumbbells , but describes time-dependent flows much more realistically.

1.6.5   Phan-Thien-Tanner model(PTT)

Originality of this model in the approach used to solve constitutive equations. They were derived using network methodology (neuron networks)

The model has only three parameters that should be found experimentally. This model can control extensional and shear response of the flow, because it includes material functions that describe these parameters.

In a most simple case this model can be solved analytically for viscometric functions.

The original model can be found in [Thien and Tanner 1977]

Here we consider its affine version. Such version describes fluid with zero SNSD, i.e where parameter that describes viscometric flow $\xi = 0$, then equation can be written:

$$Z(tr\,\boldsymbol{\tau})\boldsymbol{\tau} + \lambda \boldsymbol{\tau}_1 = -\eta_0 \dot{\boldsymbol{\gamma}} \tag{37}$$

where:

$$Z = \begin{cases} 1 - \varepsilon \lambda tr\,\tau/\eta_0 & \mathrm{L}inear\,model\,(LPTT) \\ \exp[-\varepsilon \lambda tr\,\tau/\eta_0] & \mathrm{E}xponential\,model\,(EPTT) \end{cases} \tag{38}$$

where:

η_0- viscosity

λ- the time parameter

ε- "extensional parameter"

From these equations follows that LPTT is identical to FENE-P dumbbell model in a case of simple shear flow.

Even though the FENE-P model was build using kinetic theory and PPT was build using neuron network principles, in both cases for simple shear flow was obtained identical equations [Thien and Tanner 1977].

2   Experimental part

2.1   Workflow

The laboratory work done in an iterative scheme:

First step was calculation of initial concentration of polymer to obtain desired concentration.

Second step was mixing of "stock solution" and recording real values of mass and concentration. Because these numbers will be used to make dilute concentrations. These values are presented in Tables 2, 6, 10,14, 17, 20.

Third step was to calculate amount of water and "stock solution" that will be taken to make next low concentration, real and calculated numbers saved in Tables. 4 , 8, 12, 17, 19, 21.

The fourth step was at rheometer laboratory to measure viscosity and other parameters; results of measurement was export to Tables 5, 9, 13 for further analysis.

Next steps were to identify zones of interest in Excel; calculate missing concentrations; dilute additional polymer concentrations; measure new solutions at rheometer and update Excel data file.

2.2   Polymers taken for experiment

In this work both natural and synthetic polymers were chosen.

Tested natural polymers are HEC(hydroxyethyl cellulose), Polypac(polyanionic cellulose), Xanthan gum (polysaccharide). These polymers were chosen due to relevance for oil industry and their accessibility, they can be found in the laboratory in large amounts.

Number of tests were run with laboratory polymers to get right equipment parameters and optimal solution concentrations were found.

Tested synthetic polymers is a group of Flopaams. Flopaams is a commercial name of group of polymers, in this work used 5115VHM, 5115VLM, AN125VHM, AN125VLM, 3630SVHM, 3130S. For this group equipment parameters, measurements, diluted concentrations were taken in uniform style to have a good data set for further calculations.

HEC- hydroxyethyl cellulose. Chemical formula $(\mathbf{CH_2\,CH_2\,OH})_\mathbf{n}$ It is a product of natural cellulose. It is widely used in cosmetic and household industry due to its gelling property.

In oil industry it used to improve properties of drilling fluid. To increse penetration rate of fluid and to cool down drilling bit.

It is non-ionic polymer, hence stable in salt brine. Wever, Picchioni, and Broekhuis 2011 Stability in salt brine is very important parameter in terms of work at the sea conditions.

Has high resistance to bacteria.
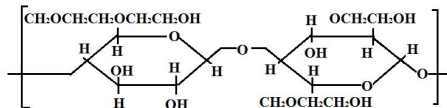
Figure 21: Structural formula of HEC

Xanthan gum- is a biological polymer 22, polysaccharide that obtained in result of fermentation (i.e by bacteria) and it is very sensitive to bacteria degradation. The chemical formula $(\mathbf{C_{35}H_{49}O_{29}})_n$

it has very high molecular weight.

It is highly dependent on temperature and this dependence is not linear. In spite of this complex behaviour polymer has lots of attractive properties.

Xanthan solutions, like all polymers, exhibit shear thinning behaviour: at high shear rates they loose viscosity.

Concentration and viscosity of Xanthan have a direct dependence: the higher concentration the higher viscosity.

It is anionic polymer with good resistance to salt water.

Xanthan is widely used in oil industry, in cosmetics and in food industry, due to its great ability to increase viscosity.

In oil industry Xanthan is used to thickening drilling mud, due to it makes mud viscous and easy to control [Garsia-Ochoa et al. 2000].
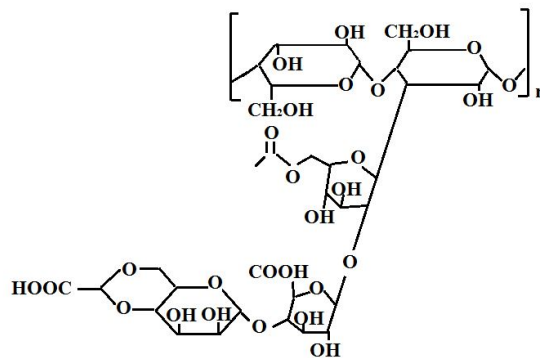
Figure 22: Structural formula of xanthan

Flopaams is a group of polyacrylamide polymers structural formula (23) In their polymerization the key element is acrylamide. The chemical formula $(\mathbf{C_3H_5NO})_n$

For experiment were available polymers from three main groups (acrylamide, co-polymers and standard) and each sample was presented in a low and high molecular weight,such that in total there are six Flopaam samples.

The structure of acrylamide monomers is called: **"random coil"**. This polymer can display electrolyte properties due to some groups of this molecule might react with solution.

The Flopaam AN 125 belongs to "co-polymers" at sulfonated polyacrylamide group. "Co-polymer" means there are two different monomers are used to make this polymer.

This group claimed to have a better thermal stability due to adding anti oxidising agents at production stage.
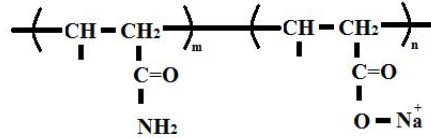
Figure 23:   Structural formula of polyacrilamide

Table 1: Flopaam main parameters

Flopaam	*Group*	*Anionicity*	*Molecular weight*
5115 VHM	Acrylamide acid polymers	Medium	Very High
3630 S VHM	standard	Medium to High	High
AN 125 VHM	co-polymers of ATBS	Medium	Very High
3130S	Standard	Medium to High	Ultra Low
AN 125 VLM	co-polymers of ATBS	Medium	Very Low
5115 VLM	Acrylamide acid polymers	Medium	Very Low

From technical description of company producing Flopaams: In dependency on production technology Flopaams are divided on three groups:

co-polymerization; co-hydrolysis; post-hydrolysis.

"Standard polymers: co-polymers of acrylamide and acrylate are suitable for reservoir with temperature up to 70° C (185°F) and 35 000 ppm, max 1000 ppm of divalent ions.

Co-polymers of ATBS and acrylamide are less sensitive to temperature and salinity. They are recommended for reservoir temperatures up to 95°C(203°F)." [SNFFloergel 2012]

2.3   Polymers mixing

Equipment:
   - mixer (with speed range 10 rpm - 1500 rpm)
   - magnetic stirrer (to mix dissolved polymers in approximate volume 50 ml)
   - beaker for mixing reagents (approximate volume 1 liter)
   - laboratory scales
   - measuring spoon

Before lab work starts the amount of polymer powder and water needed to get a certain concentration of polymer solution should be calculated.

Calculation of concentrated solution:

required mass of polymer

$$= \frac{(\text{desired concentration}) \times (\text{mass of solvent})}{(1 - \text{desired concentration})} =$$

$$= \frac{c \times M_s \times 10^{-6}}{1 - c \times 10^{-6}} \qquad \left[\frac{\text{g} \quad \text{ppm}}{\text{ppm}}\right] \tag{39}$$

real concentration

$$= \frac{(\text{measured mass of polymer})}{(\text{measured mass of polymer}) + (\text{measured mass of solvent})} =$$

$$= \frac{M_{pRe} \times 10^{-6}}{M_{pRe} + M_{sRe}} \qquad \left[\frac{\text{g} \quad \text{ppm}}{\text{g}}\right] \tag{40}$$

Calculation of diluted solution:

theoretical mass polymer

$$= \frac{\text{desired concentration}}{\text{real concentration of iniial polymer solution}} = \frac{c \times M_s}{c_0} \qquad \left[\frac{\text{g} \quad \text{ppm}}{\text{ppm}}\right] \tag{41}$$

required mass of diluted solution

$$= \frac{\text{Re mass of concentrated polymer} \times \text{Re concentration of initial polymer}}{\text{desired concentration of diluted solution}} =$$

$$= \frac{M_p \times c_o}{c_{Re}} \qquad \left[\frac{\text{g} \quad \text{ppm}}{\text{ppm}}\right] \tag{42}$$

Procedure of making polymer solution:

This section gives a description of making polymers; obtained numbers for each polymer solution are given in tables in Section: 2.5.

The amount of polymer powder and water needed for diluted solutions was calculated before start laboratory mixing. For a further convenient comparison it is necessary to have uniform concentrations and as a start point for a "stock solution" was taken 500 gram concentrated solution.

Equipment that was used in "mud-lab": laboratory scales, to weight polymer powder and water; laboratory mixer; laboratory stirrer; mixing beakers; jars to store "stock solution".

After several test for mixing a tool with two mixing blades was chosen: due to it provides proper mixing with minimum bubbles.

Polymer powder is available in big containers, a special measuring spoon to pick powder from them. Then this powder was poured on a scale plate, that was covered by paper(paper was weighted and scales was set to zero, before measure powder). To weight water a beaker was used, it was weighted, then scales set to zero, then keeping the mixing baker on the scales take another beaker and pour the desired amount of water into the mixing baker.

When water and powder was weighted the mixing beaker was set to mix, and mixer run. Mixing speed varies in according to viscosity of fluid, results are presented in Tables: 5, 9, 13.

After mixing at mixer polymer should be left at magnetic stirrer approximately for 10 hours this procedure dispose of bubbles that might appear after mixing.

When all mixing procedures were finished the polymer was pour into the jar with a cork and marked with a sticker that has information about the polymer and preparation date. Then "stock solution" stored in a fridge to keep it for a further experiments.

Dilute polymers were mixed on magnetic mixing stirrer before testing them at the rheometer.

2.4   Rheometer

There rheometer MCR-302 is available for experiments. It has several different tools that can be used for measurements.

As claimed by the rheometer manufacturer the most appropriate tool for measuring small amount of liquids is *conic plate tool*(i.e. cone and plate instrument), but it has some difficulties in measuring that corresponds to a narrow gap and trimming of liquid that runs over the measuring surface. Measurement with this tool gives *constant shear rate* due to geometry of this tool. It is why this tool is preferable.

The tool with *parallel plate* differ from conic plate only by shape of upper plate and due to upper plate is flat, gap between plates is larger, so liquid must be more viscous to avoid it running out. Due to its geometry, this tool does not provide constant shear rate, so can not be used to measure viscometric functions.

Another recommended tool to measure liquids is concentric cylinder, it is easy to use, but it should be used only for a low viscous liquids. This tool is easy to use, but difficult to measure.

Geometry of this tool allows a wide enough gap between cone and beaker, as a result at high shear rates there might occur turbulence; and at low shear rates rheometer needs a long time to get measurement at steady flow. This tool works good only for Newtonian fluids.

The rheometer is connected to a PC, allowing software to process data. Operator can display different parameters and dependencies both in graphical and table form this allows to control the process of measurement and make changes on the early stage of experiment [Mezger 2015].

Both tools: concentric cylinder and cone-plate tool was chosen for a test with two polymers: one with a high and one with a low viscosity.

The test with concentric cylinder for water-like polymer showed unstable behaviour of viscosity curve. At low shear rates the curve shows high fluctuation in the measurement that is equal to a measurement of the level of error. At high shear rates, the viscosity curve shows increasing behaviour, while for shear thinning liquids we expect this curve goes down; such behaviour can be explained by turbulence in a beaker.

Tests with cone-plate showed that measurement of liquids with low viscosity is stable at a high measuring time in interval of low shear rates.

After both tools were tested with both polymers, and with several runs on the same liquid, the decision was taken to use the cone-plate tool and start with the viscous polymer, diluting it until minimum possible measuring concentration.

Tests that was run to identify which tool shall be taken also run to choose appropriate measuring interval and equipment parameters. From such test the time interval and shear rate range was chosen: time=7 s at shear rate=200 1/s and time=60 s at shear rate =0.01 1/s. Here should be note, that this range was identified for fluids with concentration in a range 600 ppm-10 000 ppm.

But following experiments with highly diluted solutions showed that to get more

accurate numbers at low shear rates we should increase time that rheometer use to measure one point. Rheometer is measuring forces, and then calculating viscosity, and at low shear rates forces also very low, it is why measure time should be longer.

As a result for all polymer solutions with concentration less 400 ppm was chosen new range of time interval: time=20 s at shear rate=200 1/s and time=100 s at shear rate =0.01 1/s [Mezger 2015].

Main rheometer parameters

As it said in the manual to the Anton Paar software [Mezger 2015] , most of parameters that defined by rheometer are calculated during measurements and these calculations are based on principals of two-plates model, as shown in Fig. 24

The "toy model" is used to show the principle of rheological measurement. The detailed description of fluid dynamic under rheological measurment under cone/plate and plate/plate tools can be found in book [R. B. Bird 1977]

- Technical parameters

    cone angle for cone/plate tool $\alpha = 1°$

    plate diameter $d = 25mm$

    gap between plates $a = 50\mu m$

- Measured parameters

    shear rate

    time at one point

    time and shear rate are pre-set parameters, they should be chosen by operator before rotation cycle starts (always can be taken default numbers).

    Time is a time that rheometer take to make measurement at one point given range means that time or shear rate will vary gradually from one value to other with chosen step, we can take linear or logarithmic step, so we can take more points at low shear rates or vice versa.

    Measurements for one sample is a set of points at given rotation cycle.

- Calculated parameters

Shear stress is calculated parameter, and it requires to know value of shear force F and plate area A. The shear force is measured in relation with the torque. The range of torque variation should be determined by engineer before measuring.

$$\text{shear stress} \quad \tau = \frac{\text{shear force}}{\text{area}} = \frac{F}{A} \quad \left[\frac{N}{m^2}\right] \tag{43}$$
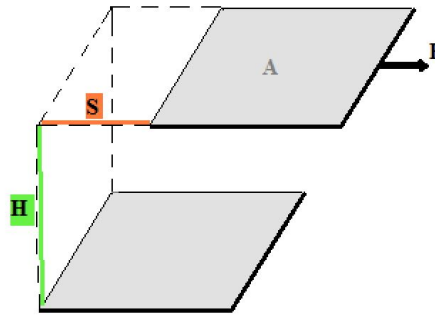
Figure 24: Two plates model

Range of shear rate and time interval needed for one measurement should be specified by engineer, depending on viscosity of liquid.

$$\text{shear rate} \quad \dot{\gamma} = \frac{\text{velocity}}{\text{shear gap}} = \frac{v}{H} \qquad \left[\frac{1}{s}\right] \qquad (44)$$

$$\text{viscosity} \quad \eta = \frac{\text{shear stress}}{\text{shear rate}} = \frac{\tau}{\dot{\gamma}} \qquad \left[\frac{Pa}{s}\right] \qquad (45)$$

2.5   Overview of laboratory data

HEC (hydroxyethyl cellulose).

For a test was taken concentration 15 000 ppm polymer solution in distilled water

$$(15\,000 \,*\, 100\,\%)/1\,000\,000 \,=\, 1,5\,\% \tag{46}$$

Table 2: Measured and calculated amount of HEC and solution

Polymer	Desired concentration [ppm]	Required mass of water [g]	Required mass of polymer [g]	Measured mass of polymer [g]	Measured mass of solvent [g]	True concentration of polymer [ppm]
HEC	15 000	450	6.89	6.86	452.45	14 935.45

Table 3: Equipment parameters (mixer and magnet) for HEC

Polymer	Time mix	Rotation Frequency [rpm]	Additional info	Magnet rotation [rpm]	Magnet Time
HEC	start 11:36	763	adding polymer powder to water	450	start 14:00 (6march)
	end 13:45	700	after adding polymer	400	end 11:10 (7march)

The solution with concentration 0.3% was mixed on magnet 20 min, with a speed of 1000 but had a significant amount of bubbles (probably due to high speed); an attempt was made to remove the bubbles using vacuum pump, but it broke down the bubbles into smaller sizes, so the overall amount of bubbles had increased, then the

Table 4: Diluted solutions of polymer (HEC)

Solu-tion	Desired Con-centra-tion [ppm]	Calc mass poly-mer [g]	Calc mass total [g]	Measured mass polymer [g]	New theor mass total [g]	New mea-sured mass total [g]	Magnet rota-tion [rpm]	Real concen-tration [ppm]
HEC 1.5%	12 000	40.17	50	40.16	49.98	50.04	1 200	11 986.5
	9 000	30.13	50	30.37	50.39	50.39	1 200	9 001.55
	6 000	20.09	50	21.45	53.39	53.40	1 000	5 999.33
	3 000	10.0	50	9.86	49.09	49.14	850	2 996.81

solution was left on magnet for additional 20 min, with a speed 450. After that it was stored in a fridge for 10 hours and then measured in rheometer.

Recommendation: do not use vacuum to remove any bubbles, and for low viscosity liquids use slower speed on the magnet.

Rheometer parameters:
Every new set of measurements starts with commands:
Set temperature; Reset normal forces

Table 5: Rheometer parameters, HEC

Parameter	Range	Additional informa-tion
Temperature	20 °C	
Range of Shear Rate	0.01-200 1/s	
Length of time for one measurement at one points	shear rate 200/s at time 7 s	measurement for the same point is recorded twice: while increasing shear rate and while decreasing shear rate
	shear rate 0.01/s at time 60 s	

Xanthan gum.

For a test was taken concentration 10 000 ppm polymer solution in distilled water

$$(10\,000 * 100\,\%)/1\,000\,000 = 1\,\% \tag{47}$$

Table 6: Measured and calculated amount of Xanthan and solution

Polymer	Desired concentration [ppm]	Required mass of water [g]	Required mass of polymer [g]	Measured mass of polymer [g]	Measured mass of solvent [g]	True concentration of polymer [ppm]
Xanthan	10 000	450	4.56	4.54	451.47	9 955.92

Table 7: Equipment parameters (mixer and magnet) for Xanthan

Polymer	Time mix	Mixer Rotation frequency [rpm]	Additional info	Magnet rotation [rpm]	Magnet Time
Xanthan	start 16:25	560	adding polymer powder to water	magnet is not able to rotate solution due to high viscosity of polymer	start 19:00 (8march)
	end 18:45	500	after adding polymer	left at mixer with speed 150	end 12:10 (9march)

Table 8: Diluted solutions of polymer (Xanthan)

Solu-tion	Desired Con-centra-tion [ppm]	Calc mass poly-mer [g]	Calc mass total [g]	Measured mass polymer [g]	New theor mass total [g]	New mea-sured mass total [g]	Magnet speed [rpm]	Real concen-tration [ppm]
1.0%	8 000	40.16	50	40.18	49.98	50.20	700	7 968.7
	6 000	30.13	50	30.66	50.87	51.27	700	5 953.75
	4 000	20.09	50	20.87	51.95	52.10	700	3 988.1
	2 000	10.04	50	9.19	45.75	46.05	700	1 986.86
	1 000	5.00	50	5.01	49.87	49.96	500	998.38
	500	2.50	50	2.45	48.78	48.93	200	498.51
	100	1.00	50	1.08	107.53	107.54	200	99.99

Table 9: Rheometer parameters, Xanthan

Parameter	Range	Additional informa-tion
Temperature	20 °C	
Range of Shear Rate	0.01-200 1/s	
Length of time for one measurement at one points	shear rate 200/s at time 7 s	measurement for the same point is recorded twice: while increasing shear rate and while decreasing shear rate
	shear rate 0.01/s at time 60 s	

Group of FLOPAAM polymers is taken with the initial solution concentration 10 000 ppm and equal steps between concentrations in diluted solutions for a convenient graphical analysis of their behaviour.

Tables " Equipment parameters (mixer and magnet)" and "Rheometer parameters" have similar parameters for all polymers of group Flopaam.

FLOPAAM 5115 VHM

For a test was taken concentration 10 000 ppm polymer solution in distilled water

$$(10\,000 * 100\,\%)/1\,000\,000 = 1\,\% \tag{48}$$

Table 10: Measured and calculated amount of Flopaam 5115 VHM and solution

Polymer	Desired concentration [ppm]	Required mass of water [g]	Required mass of polymer [g]	Measured mass of polymer [g]	Measured mass of solvent [g]	True concentration of polymer [ppm]
Flopaam 5115VHM	10 000	450	4.56	4.54	450.50	9 977.14

Note: number of rheometer test showed that solutions with a low polymer concentration at low shear rate should be measured at longer time interval than solutions with high concentration;

time was chosen 100 s for a shear rate 0.011/s and 20 s for shear rate 200 1/s.

Table 11: Equipment parameters (mixer and magnet) for Flopaam group

Polymer	Time mix	Rotation frequency [rpm]	Additional info	Magnet rotation [rpm]	Magnet Time
Flopaaam 5115VHM	start 12:30	450	adding polymer powder to water	magnet is not able to rotate solution due to high viscosity of polymer	start 14:45 (13march)
	end 14:30	400	after adding polymer	left at mixer with speed 120	end 10:10 (14march)
Parameters in this table are similar for all Flopaams					

Table 12: Diluted solutions of polymer (Flopaam 5115VHM)

Solution	Desired Concentration [ppm]	Calc mass polymer [g]	Calc mass total [g]	Measured mass polymer [g]	New theor mass total [g]	New measured mass total [g]	Magnet rotation [rpm]	Real concentration [ppm]
	8 000	40	50	41.27	51.59	51.37	450	8 033.87
	6 000	30	50	29.32	48.87	48.92	450	5 993.46
	4 000	20	50	19.58	48.95	49.55	450	3 951.56
	2 000	10	50	10.50	52.50	52.15	450	2 014.58
1.0%	1 000	5	50	5.52	55.20	55.28	450	998.55
	800	4	50	3.76	47.00	46.94	450	801.02
	600	3	50	2.93	48.83	48.10	450	609.15
	400	2	50	1.93	48.25	48.30	450	399.59
	300	2.39	80	2.36	78.82	76.06	200	299.09
	200	1.59	80	1.58	79.15	80.17	200	197.45
	100	0.79	80	0.78	78.15	78.10	200	100.07

Table 13: Rheometer parameters, Flopaam 5115 VHM

Parameter	at concentration 0.1-0.04%	at concentration 0.03-0.01%	Additional information
Temperature	20 °C	20 °C	
Range of Shear Rate	0.01-200 1/s	0.01-200 1/s	
Length of time for one measurement at one points	shear rate 200/s at time 7 s	shear rate 200/s at time 20 s	Measurement for the same point is recorded twice: while increasing shear rate and while decreasing shear rate
	shear rate 0.01/s at time 60 s	shear rate 0.01/s at time 100 s	
Parameters in this table are similar for all Flopaams			

FLOPAAM 3630S VHM

For a test was taken concentration 10 000 ppm polymer solution in distilled water

$$(10\,000 \, * \, 100\,\%)/1\,000\,000 \, = \, 1\,\% \tag{49}$$

Table 14: Measured and calculated amount of Flopaam 3630S VHM and solution

Polymer	Desired concentration [ppm]	Required mass of water [g]	Required mass of polymer [g]	Measured mass of polymer [g]	Measured mass of solvent [g]	True concentration of polymer [ppm]
Flopaam 3630S VHM	10 000	450	4.55	4.55	450.92	9 989.68

Table 15: Diluted solutions of polymer (Flopaam 3630S VHM)

Solution	Desired Concentration [ppm]	Calc mass polymer [g]	Calc mass total [g]	Measured mass polymer [g]	New theor mass total [g]	New measured mass total [g]	Magnet rotation [rpm]	Real concentration [ppm]
	8 000	40.04	50	39.64	49.55	49.30	450	8 040.57
	6 000	30.03	50	28.49	47.48	47.25	450	6 029.63
	4 000	20.03	50	21.71	54.23	54.39	450	3 991.54
	2 000	10.01	50	11.15	55.75	55.22	450	2 019.20
1.0%	1 000	5.01	50	5.22	52.20	52.20	450	1 000
	900	4.50	50	4.46	49.50	49.48	450	900.44
	800	4.00	50	3.97	49.63	49.49	450	802.18
	700	3.51	50	3.58	51.09	51.11	450	699.73
	600	3.00	50	3.03	50.50	50.30	450	602.39
	500	2.50	50	2.49	49.75	49.56	450	501.90
	400	2.00	50	2.18	54.50	54.06	450	403.26
	300	2.40	80	2.25	74.92	74.91	200	300.05
	200	1.60	80	1.62	80.92	80.80	200	200.23
	100	0.80	80	0.87	86.91	87.22	200	99.65

FLOPAAM AN 125 VHM

For a test was taken concentration 10 000 ppm polymer solution in distilled water

$$(10\,000 \,*\, 100\,\%)/1\,000\,000 \,=\, 1\,\% \tag{50}$$

Table 16: Measured and calculated amount of Flopaam AN 125 VHM and solution

Polymer	Desired concentration [ppm]	Required mass of water [g]	Required mass of polymer [g]	Measured mass of polymer [g]	Measured mass of solvent [g]	True concentration of polymer [ppm]
Flopaam An 125 VHM	10 000	450	4.55	4.50	450.49	9 890.33

Table 17: Diluted solutions of polymer (Flopaam AN 125 VHM)

Solution	Desired Concentration [ppm]	Calc mass polymer [g]	Calc mass total [g]	Measured mass polymer [g]	New theor mass total [g]	New measured mass total [g]	Magnet rotation [rpm]	Real concentration [ppm]
	8 000	40.44	50	38.81	47.98	48.97	200	7 838.34
	6 000	30.33	50	28.23	46.53	47.56	200	5 878.56
	4 000	20.22	50	18.53	46.82	46.45	200	3 945.49
	2 000	10.11	50	9.96	49.25	49.67	200	1 983.24
	1 000	5.06	50	5.05	49.94	50.39	200	991.19
1.0%	800	4.04	50	4.07	50.32	51.22	200	785.89
	600	3.03	50	2.77	45.66	46.42	200	590.19
	400	2.02	50	1.94	48.71	48.64	200	400.32
	300	2.42	80	2.34	78.13	79.30	200	295.59
	200	1.61	80	1.54	76.15	77.26	200	197.14
	100	0.81	80	0.73	72.20	73.26	200	98.55

FLOPAAM 3130S

For a test was taken concentration 10 000 ppm polymer solution in distilled water

$$(10\,000 * 100\,\%)/1\,000\,000 = 1\,\% \tag{51}$$

Table 18: Measured and calculated amount of Flopaam 3130S and solution

Polymer	Desired concentration [ppm]	Required mass of water [g]	Required mass of polymer [g]	Measured mass of polymer [g]	Measured mass of solvent [g]	True concentration of polymer [ppm]
Flopaam 3130S VHM	10 000	450	4.55	4.56	451.92	10 032.90

Table 19: Diluted solutions of polymer (Flopaam 3130S)

Solution	Desired Concentration [ppm]	Calc mass polymer [g]	Calc mass total [g]	Measured mass polymer [g]	New theor mass total [g]	New measured mass total [g]	Magnet rotation [rpm]	Real concentration [ppm]
	8 000	39.86	50	39.62	49.69	49.69	200	7 999.67
	6 000	29.98	50	29.25	48.91	48.76	200	6 081.50
	4 000	19.93	50	19.15	48.03	48.26	200	3 981.40
	2 000	9.97	50	9.48	47.55	47.61	200	1 999.73
1.0%	1 000	4.98	50	5.19	52.07	52.28	200	995.99
	800	3.98	50	4.06	50.92	51.02	200	798.38
	600	2.99	50	2.92	48.83	48.86	200	599.59
	400	1.99	50	2.05	51.42	51.42	200	399.98
	300	2.39	80	2.35	78.59	78.63	200	299.85
	200	1.59	80	1.57	78.76	78.72	200	200.09
	100	0.79	80	0.80	80.26	80.23	200	100.04

FLOPAAM AN 125 VLM
For a test was taken concentration 10 000 ppm polymer solution in distilled water

$$(10\,000 * 100\,\%)/1\,000\,000 = 1\,\% \tag{52}$$

Table 20: Measured and calculated amount of Flopaam AN 125 VLM and solution

Polymer	Desired concentration [ppm]	Required mass of water [g]	Required mass of polymer [g]	Measured mass of polymer [g]	Measured mass of solvent [g]	True concentration of polymer [ppm]
Flopaam AN 125 VLM	10 000	450	4.55	4.53	449.53	10 019.60

Table 21: Diluted solutions of polymer (Flopaam AN 125 VLM)

Solution	Desired Concentration [ppm]	Calc mass polymer [g]	Calc mass total [g]	Measured mass polymer [g]	New theor mass total [g]	New measured mass total [g]	Magnet rotation [rpm]	Real concentration [ppm]
	8 000	39.92	50	38.45	48.16	48.30	200	7 676.27
	6 000	29.94	50	29.9	49.93	49.89	200	6 004.93
	4 000	19.96	50	20.09	50.32	50.42	200	3 992.34
	2 000	9.98	50	9.95	49.85	49.93	200	1 996.70
	1 000	4.99	50	4.98	49.89	49.86	200	1 000.75
1.0%	800	3.99	50	3.95	49.47	49.63	200	797.45
	600	2.99	50	2.98	49.76	49.78	200	599.87
	400	1.99	50	1.96	49.09	49.30	200	398.35
	300	2.39	80	2.39	79.82	79.83	200	299.97
	200	1.59	80	1.56	78.15	78.13	200	200.06
	100	0.79	80	0.79	79.15	79.22	200	99.92

FLOPAAM 5115 VLM

For a test was taken concentration 10 000 ppm polymer solution in distilled water

$$(10\,000 * 100\,\%)/1\,000\,000 = 1\,\% \tag{53}$$

Table 22: Measured and calculated amount of Flopaam 5115 VLM and solution

Polymer	Desired concentration [ppm]	Required mass of water [g]	Required mass of polymer [g]	Measured mass of polymer [g]	Measured mass of solvent [g]	True concentration of polymer [ppm]
Flopaam 5115 VLM	10 000	450	4.55	4.55	449.56	10 019.16

Table 23: Diluted solutions of polymer (Flopaam 5115 VLM)

Solution	Desired Concentration [ppm]	Calc mass polymer [g]	Calc mass total [g]	Measured mass polymer [g]	New theor mass total [g]	New measured mass total [g]	Magnet rotation [rpm]	Real concentration [ppm]
	8 000	39.92	50	39.74	49.77	49.79	200	7 997.17
	6 000	29.94	50	29.97	50.05	50.07	200	5 997.35
	4 000	19.96	50	19.97	50.02	50.11	200	3 993.04
	2 000	9.98	50	10.01	50.15	50.32	200	1 993.17
1.0%	1 000	4.99	50	4.94	49.49	49.48	200	1 000.34
	800	3.99	50	4.03	50.47	50.53	200	799.12
	600	2.99	50	2.98	49.76	49.82	200	599.33
	400	1.99	50	2.03	50.85	50.86	200	399.92
	300	2.39	80	2.36	78.82	79.06	200	299.09
	200	1.59	80	1.58	79.15	80.17	200	197.47
	100	0.79	80	0.78	78.15	78.10	200	100.07

3 Analysis of obtained data

The most convenient analysis of obtained data is a graphical presentation of existing relations between measured parameters. During such analysis a number of points with anomaly behaviour was chosen, and to confirm these points the measurements were carried out again. The repeated measurements showed random character of that anomaly points.

It was also defined, that measurements for polymers with a very low concentration tend to give less stable results than measurements of polymers with high concentration. The term "very low" in these experiments means concentrations below 1 000 ppm. For the majority of low concentrated samples measurements were taken after several rheometer runs with the same sample and under the same conditions, due to only under such circumstances it was possible to get stable curves behaviour.

Special effort was taken in identifying the zero-shear rate viscosity region and power law regions. To identify linear region of viscosity curve there are number of additional polymer solutions were diluted and measured at the rheometer.

Here should be reminded, that this work is a part of one big project, where we are trying to identify a model that describes polymer behaviour best. Many of existing models give good prediction for a "very dilute polymers", because region, where polymers have very low concentration, shows linear behaviour. Unfortunately, there is no exact practical definition of what polymer can be assumed "very dilute". After number of tests and graphical analysis of Fig. 35, 36, 38, 40, 42, 44, 48, I came to the conclusion that every polymer has its own number, where all concentrations below that number can be considered as "very dilute polymers". For most of polymers tested within this work such minimal concentration was 1 000 ppm. This information will be used in the Section 3.2

Measurements that was run at rheometer within this work gave a good number of data to plot dependencies and identify representative regions.

Several non-Newtonian fluid models like and FENE-P models are designed to describe very dilute solutions. In contrast, PPT model is designed to describe concentrated models. With idea to test both types of models the are number of solutions with low and high concentrations were tested.

3.1 General trends

Here are presented summary graphs of viscosity vs shear rate and viscosity vs concentration for all tested polymers their description and conclusions about flow behaviour.

The laboratory work started with HEC, Polypac and Xahnthan solutions. They were used as test-polymers to formulate a procedure for further work.

On these polymers were tested different initial and diluted concentrations, identified informative step between next diluted concentrations and range of solution concentrations. As a result these test-polymers have disbalance in measuring points

48

that leads to difficulty in numerical analysis. However it is still possible to use these data for a qualitative analysis. Due to limited time it was decided to keep laboratory polymers within tested range 10 000 - 1 000 ppm and not make very low concentrations. While Flopaam group was diluted up to 100 ppm.

The group of Flopaam polymers was tested after appropriate equipment parameters and reasonable concentration range was established. In result was obtained more uniform set of data that is easy to interpret and use for further calculations.

The plot Fig.25 is illustrating a dependency of viscosity vs shear rate at examples with different polymers and their diluted solutions.
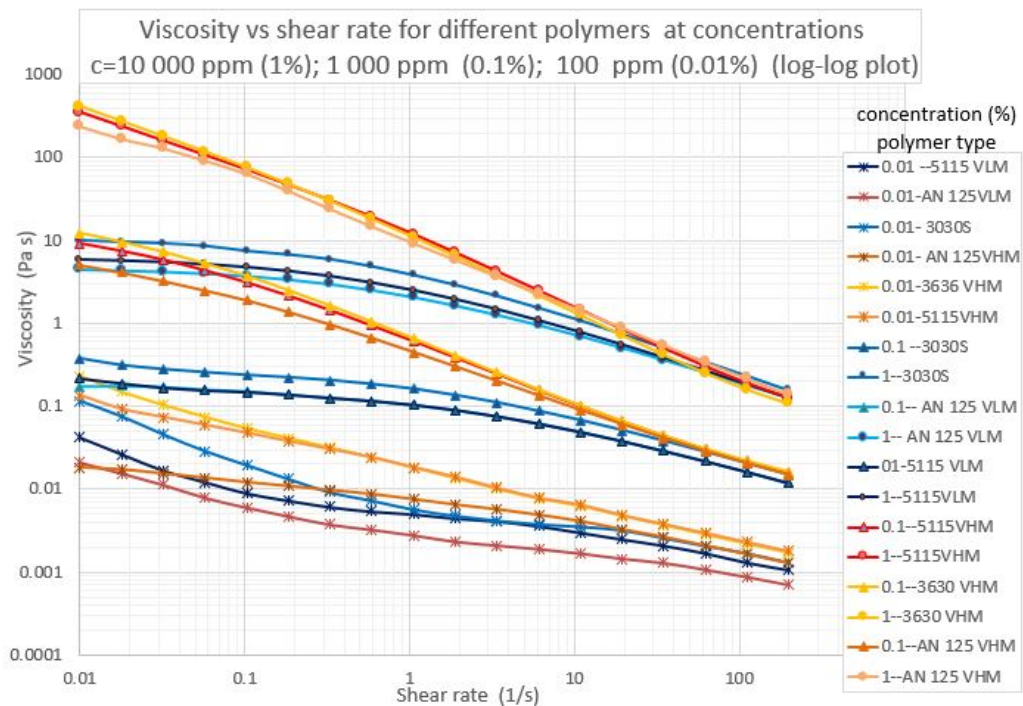
Figure 25: Viscosity vs shear rate for different polymers at concentrations 10 000 ppm, 1 000 ppm, 100 ppm

Even though this plot is very busy, five series of curves can be identified. Analysis of these curves showed that they have similar concentrations and close molecular weight. For instance:

one group is presented by polymers with VHM (very high molecular weight), which at the same time corresponding to low concentrations;

another group is presented by polymers with VHM and with high concentrations;

the third group is presented by polymers with VLM (very low molecular weight) and at the same time it corresponds to high concentrations;

fourth group is a group of polymers with VLM and low concentration and last group is a group for highly diluted solutions.
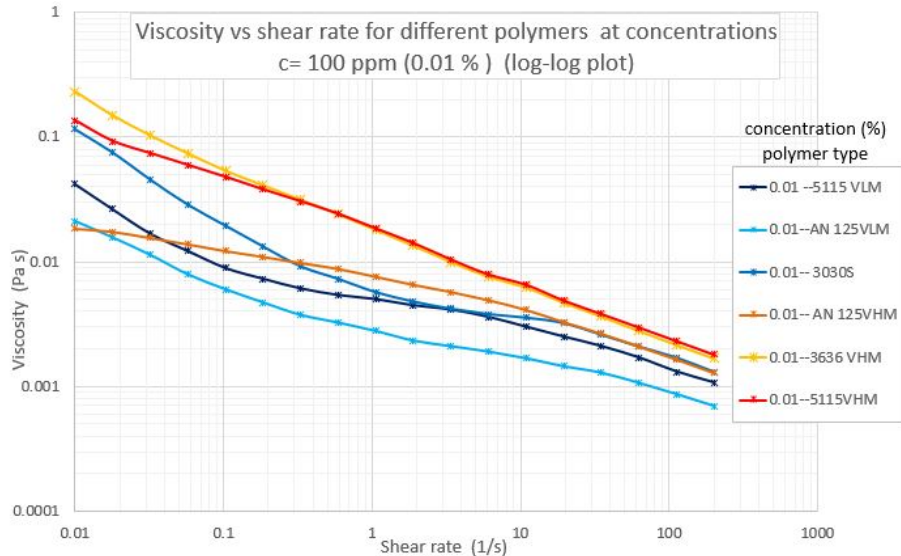
Figure 26: Viscosity vs shear rate for different polymers at concentration 100 ppm

When these trends was identified the detailed plots for each group was built.

Though in Fig. 26 shown a set of curves that expressed high fluctuation. This is a plot of viscosity vs shear rate with curves for all polymers at concentration = 100 ppm (i.e. highly dilute solutions).

Analysing this plot it is good to remember, that less precision is obtained at low shear rates for solutions with concentration below 800 ppm, due to rheometer is measuring torque, and for very dilute solutions it has a very small values, so equipment require longer measuring time at one point.

From this plot is clear, that curves at small shear rates, less than 1 $[1/s]$, display unreasonable increase in viscosity and it can be explained by a low ability to get accurate measurements at very low concentrations.

Next two plots 27, 28, shows dependency of viscosity vs shear rate for different polymers that have equal concentration. Plots are presented in log-log scale.

These plots shows set of curves with identical concentration. Fig. 27 shows curves for concentration c=1 000 ppm and Fig. 28 shows curves for concentration c= 10 000 ppm. It is clearly seen that curves on both plots exhibit identical behaviour. On both plots curves with high molecular weight have a long linear region, while curves with very low molecular weight have better pronounced zero-shear rate viscosity region. It could be due to curves with high concentrations have not reached zero-shear rate viscosity region at chosen shear-rate interval. Both plots show that points from curves presenting different polymers with different molecular weights tend to line up.
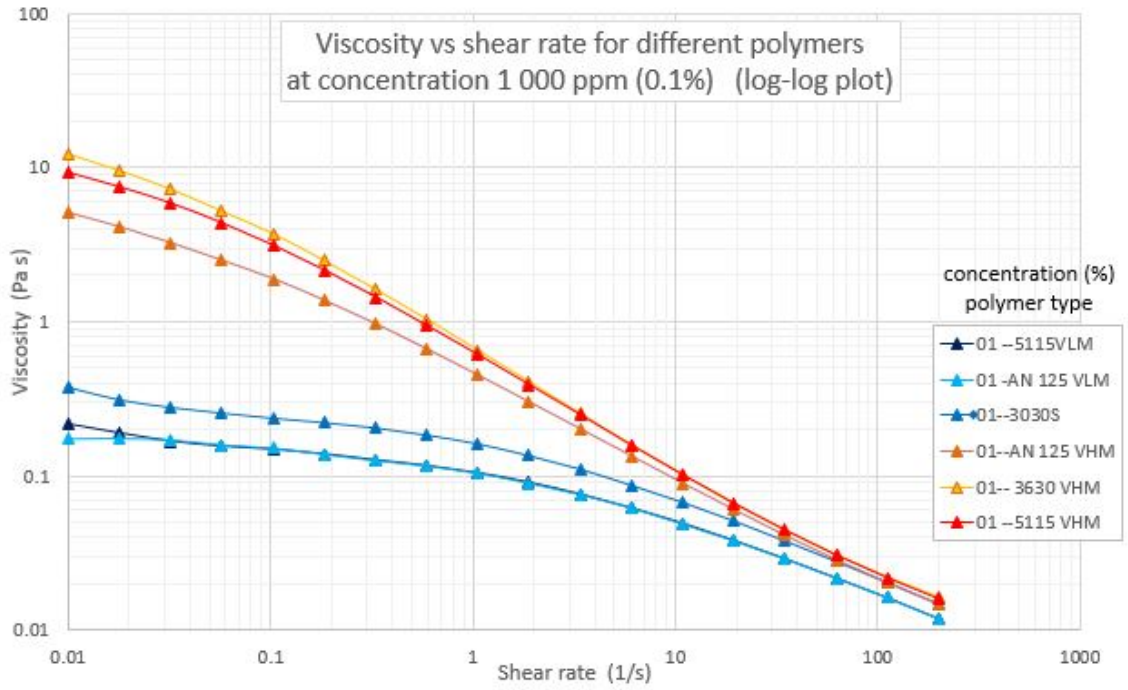
Figure 27: Viscosity vs shear rate for all polymers at concentration 1 000 ppm
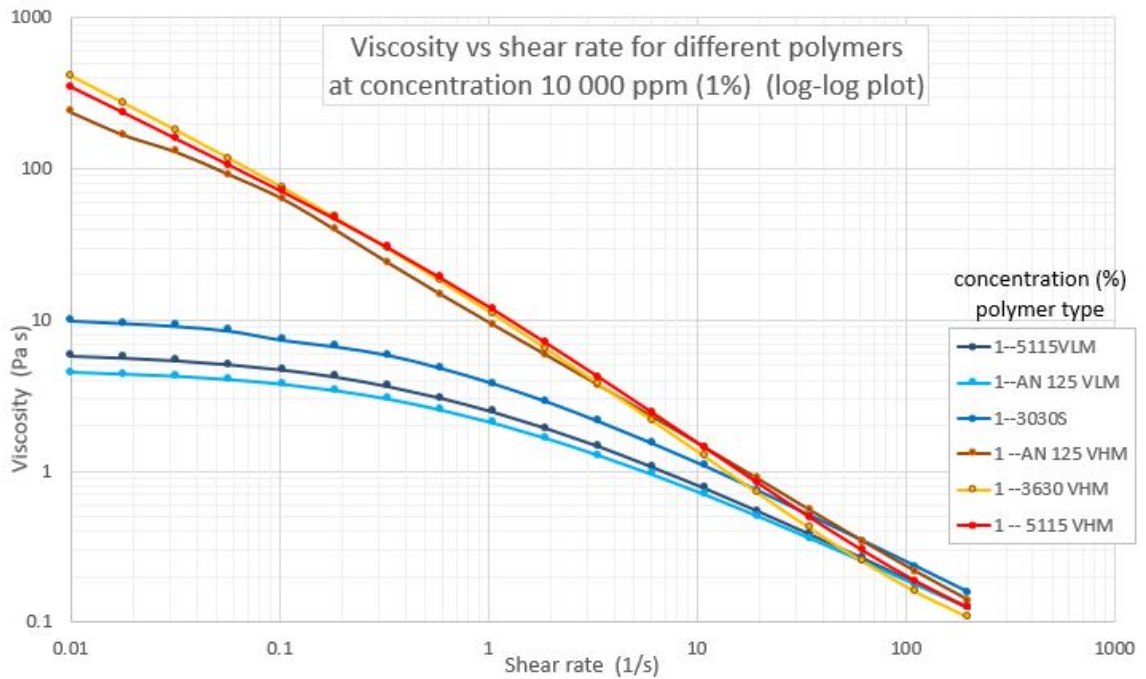
Figure 28: Viscosity vs shear rate for all polymers at concentration 10 000 ppm

Plots 29 and 30 are illustrate dependency of viscosity vs shear rate for group of VLM and VHM polymers that have equal concentrations.

Both plots show three series of curves. These series separate in accordance to their concentration.It means. that concentration is very valuable perimeter for rheological properties and it could be that properties of molecules play not so essential role as concentration.

There are series of concentration 10 000 ppm, 1000 ppm and 100 ppm. On both plots curves that represent highest concentration are located closer to each other and the lower concentration the more difference between curves inside one set.

There are two more identical tendencies: curves at high shear rates show almost equal values, while at small shear rates curves are deviate.

Both these tendencies can be explained by log-log scale. At logarithmic scale small visual difference can be high numerical difference, and vice versa.

Another trend that keeps to be observed is a linear region the slope of curves and plateau at very low shear rates. For polymers with high molecular weight linear region is longer and better pronounced, while plateau region is longer and better pronounced for polymers with low molecular weight. These trends are completely correspond to theory described by FENE-P chain model. The more beads are in the polymer molecule, the longer chain that represents this molecule, hence higher molecular weight (it was discussed in Section. 1.6.4)

As a summary, analysis of plots 27, 28, 29, 30 confirm trends identified in Fig.25.
They are:

- strongly marked separation dependent on concentration and molecular weight;

- good pronounced linear slop region for VHM and plateau region for VLM polymers;

- high fluctuation in curves with very low concentration at shear rate less than 1 $[1/s]$.
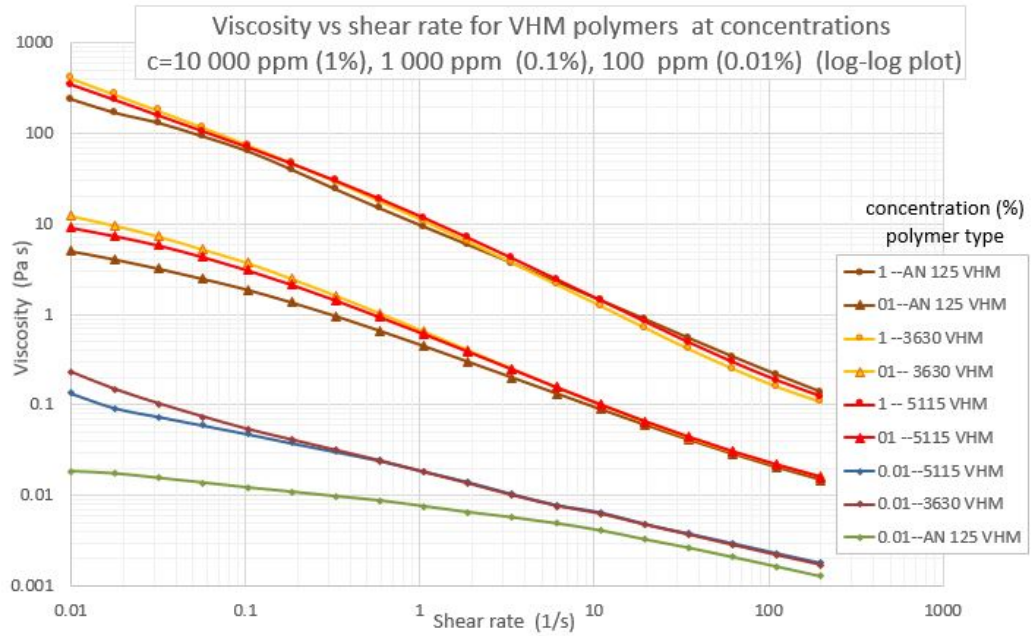
Figure 29: Viscosity vs shear rate for group of polymers with very high molecular weight (VHM) at concentrations 10 000 ppm,1 000 ppm, 100 ppm
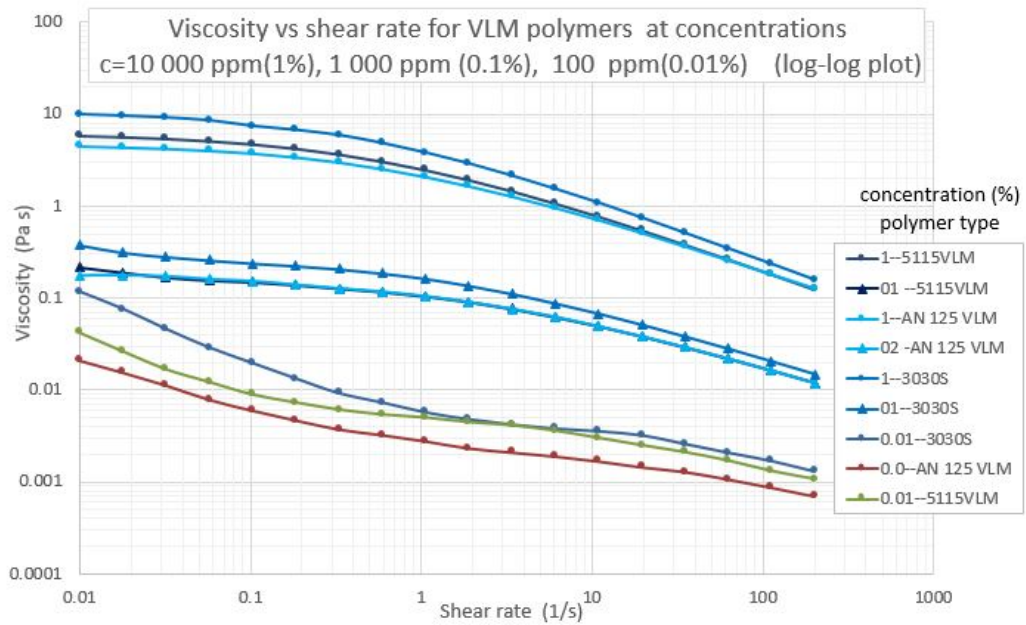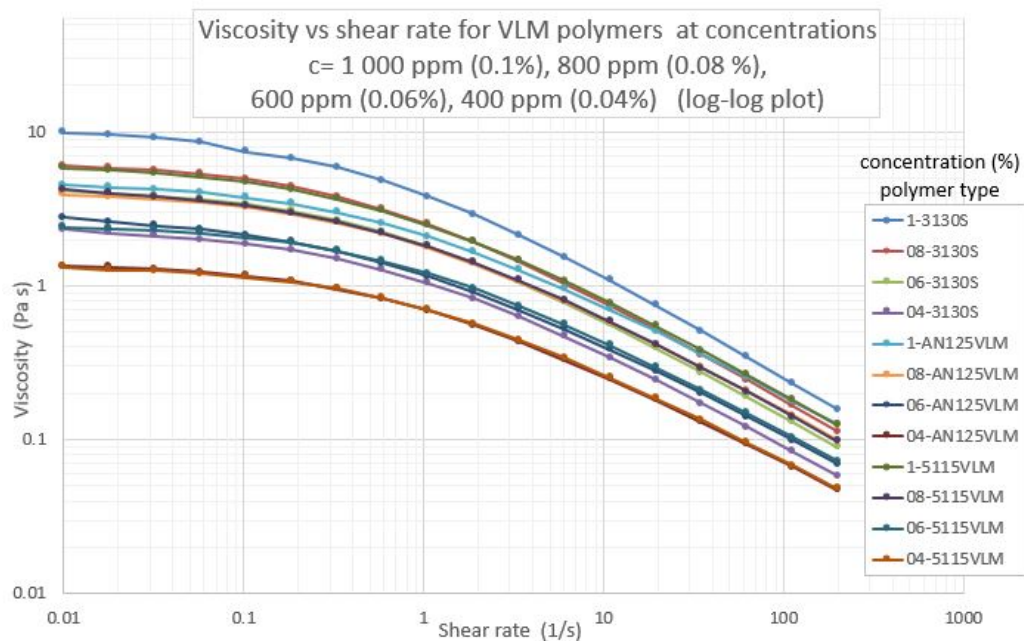

Figure 30: Viscosity vs shear rate for group of polymers with very low molecular weight (VLM) at concentrations 10 000 ppm,1 000 ppm, 100 ppm

To confirm that these trends are identical for all polymers the analogical plots was built for HEC, Poly-Pack and Xanthan. In Fig. 31 and 32 viscosity vs shear rate at different concentrations for Xanthan and HEC.
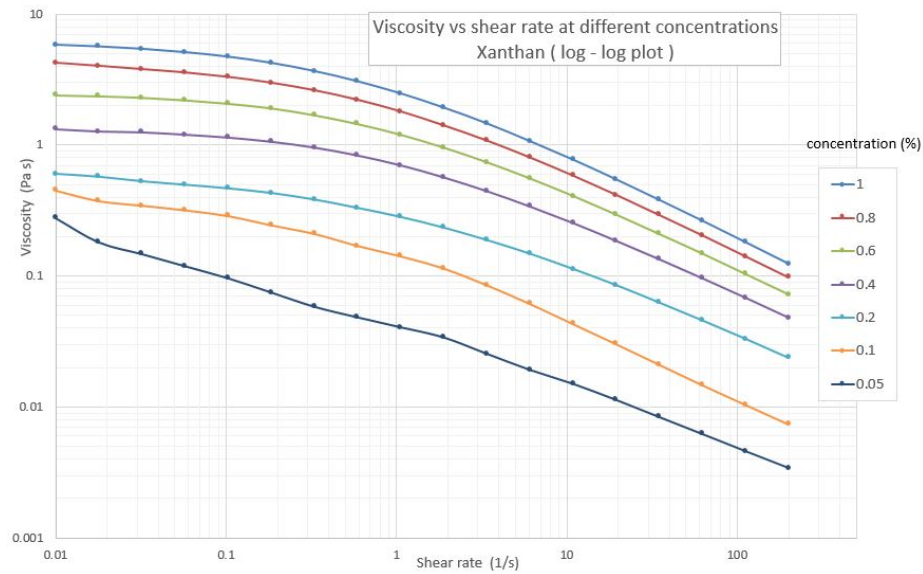
Figure 31: Viscosity vs shear rate at different concentrations, Xanthan
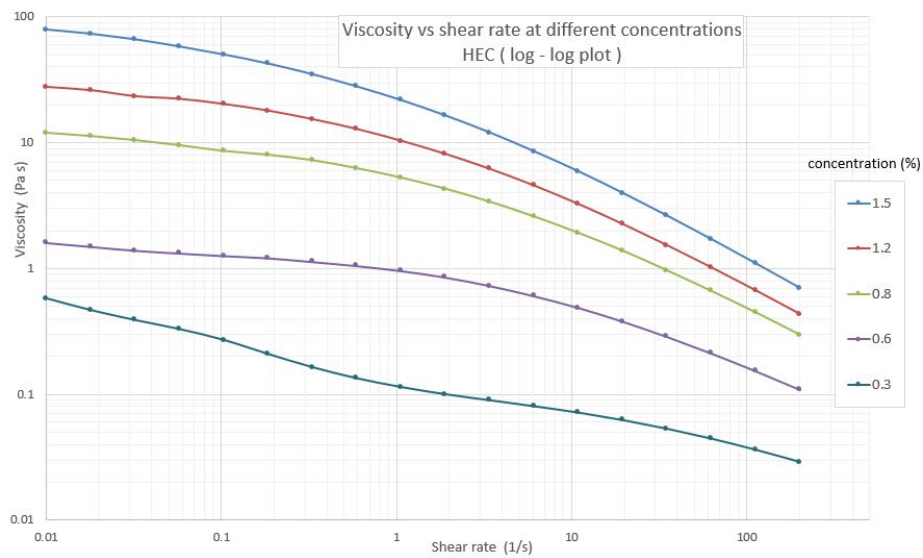
Figure 32: Viscosity vs shear rate at different concentrations, HEC

These plots show similar trends that was identified for Flopaam group. Due to Xanthan and HEC were test-polymers, seems, during our experiments were not reached concentrations of highly diluted solutions.

As expected, it confirmed problems that was observed for the low concentration Flopaams; such as difficulty to get stable measurement and not reasonable increase in Viscosity measurements for shear rate less than 1 $[1/s]$. As was discussed , due to at low shear rates torque forces are also very small the rheometer require longer time to make precise measurements.

In order to get a more complete picture of relations between viscosity and shear rate, plots with a wider range of different concentrations for polymers with similar molecular weight was built. For instance Fig. 33 has Flopaams VLM group (AN 125 VLM, 5115 VLM, 3130S) at concentrations 1 000 ppm, 800 ppm, 600 ppm, 400 ppm; and plot with identical concentrations for Flopaams VHM Fig. 34 These plots also confirm conclusion that solutions with similar molecular weight and close concentration follow the same trend.

Figure 33: Viscosity vs shear rate for group of polymers with very low molecular weight (VLM) at concentrations 1 000 ppm, 800 ppm, 600 ppm, 400 ppm
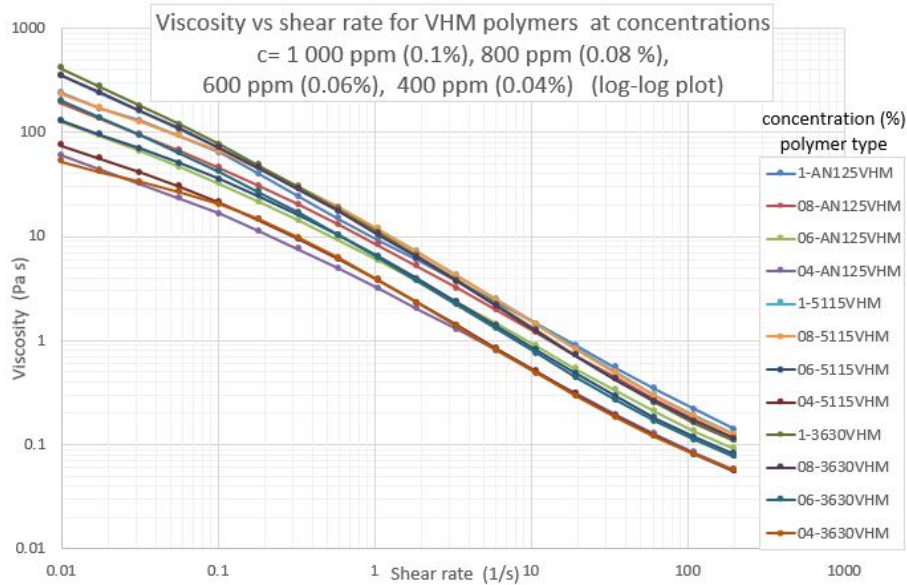
Figure 34: Viscosity vs shear rate for group of polymers with very high molecular weight (VHM) at concentrations 1 000 ppm, 800 ppm, 600 ppm, 400 ppm

Summary to plots 33 and 34: Flopaams inside group and according to their concentration show identical behaviour.

Next step is to analyse relations between viscosity, shear rate for one polymer within a wide range of concentrations. Figures 31, 32, 35, 36 show relation viscosity vs shear rate at different concentrations and viscosity vs concentration at different shear rates for polymers Xanthan and HEC.

As was shown in Fig.31 viscosity vs shear rate for Xanthan and in Fig. 32, they display similar with Flopaam group behaviour: wider variance of viscosity values for a low shear rates and small range for a high shear rates. Curve with a low concentration on both plots follow main trend, but has significant deviation. These graphs are in log-log scale and might not express all details, so it is reasonable to plot these relations in a linear scale.

Fig. 35 and 36 shows relation viscosity vs concentration at different shear rates for Xanthan and HEC. There are two main similarity in shape of curves: on both plots maximal viscosity corresponds with a maximum concentration and low shear rate, such behaviour correlates well with polymers properties. Another important feature is a linear region at low concentrations. These figures gives a visual illustration of the term "highly diluted". This linear region is well pronounced in Fig. 36 with HEC solutions. Curves are following zero line after concentration 5 000 ppm. Similar trend can be observed in Fig. 35 for Xanthan, even though it does not have very low concentrations, but it is possible to see that after concentration at 1 000 ppm all curves tend to go to zero line.

More over, analysis of similar plots for Flopaam group 38 , 48 , 44, 40 show that they also have this linear behaviour in a region with concentration less then 1 000 ppm.

Here, for a full analysis of flow behaviour, two figures are presented on one page. One figure is a plot of viscosity vs shear rate at different concentrations (in log-log scale) and another figure is a plot viscosity vs concentration at different shear rates. Such presentation helps to compare features that was identified on one plot with analogue concentration or shear rate on another plot. During laboratory measurement in such comparison regime were identified several anomalies. To confirm it or break it the additional concentrations was made and repeated measurements were run. Detected anomalies were not confirmed. Final plots have curves that exhibit similar trends.

Main tendency on plots viscosity vs shear rate is high viscosity at low shear rate and high fluctuation of low concentration curves. This variable behaviour for low concentrations is observed for shear rates less than 1 $[1/s]$ both for Flopaams and for laboratory polymers.

Plots viscosity vs concentration at different shear rates 31, 32, 36,37, 39 41 display two regions: one is a region at very high concentrations where viscosity gives high values; another well pronounced trend corresponds with a linear dependency viscosity vs concentration at very low concentrations. Such behaviour is noted as for Flopaam group as for test-polymer group.

Difference is observed in numbers; for Flopaams a border value of concentration for the upper region might be taken at 8 000 ppm, the same value display Xanthan, but HEC has upper border at 12 000 ppm. Linear trend at low concentrations for HEC starts at concentration below 6 000 ppm, while for Xanthan it should be at concentration less than 4 000 ppm. The same can be said about Flopaam group, all of them have minimum values of viscosity at very low concentrations, less then 1 000 ppm. So we can say about uniform trend for all tested polymers.

A summary to this chapter:

Analysis of plots confirmed well known trends, namely separation of polymers by molecular weight and concentration;high viscosity at low shear rates; linear region on a slop and plateau at low shear rates.

The question, asked at the beginning of this work was answered: what are "very dilute" polymers. It can be explained physically as a region where viscosity is linear in concentration at low shear rates. This requires to identify such region.

Number of measurements was focused on low concentrations and plots were built to identify it.

The linear trend at low concentrations was identified. Analysis of graphs for all tested polymers showed that concentration from which the polymer might be considered as a very dilute is unique for different polymers. It means that before any model will be run to predict flow behaviour it is necessary to run experiments and identify in what range this polymer is very dilute.
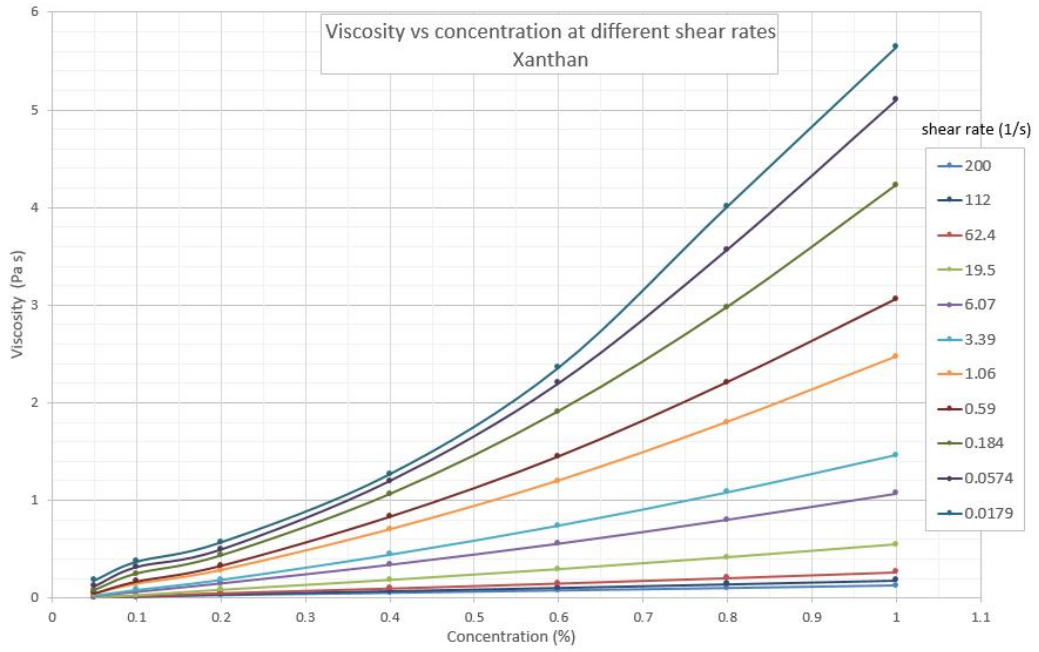
Figure 35: Viscosity vs concentration at different shear rates, Xanthan
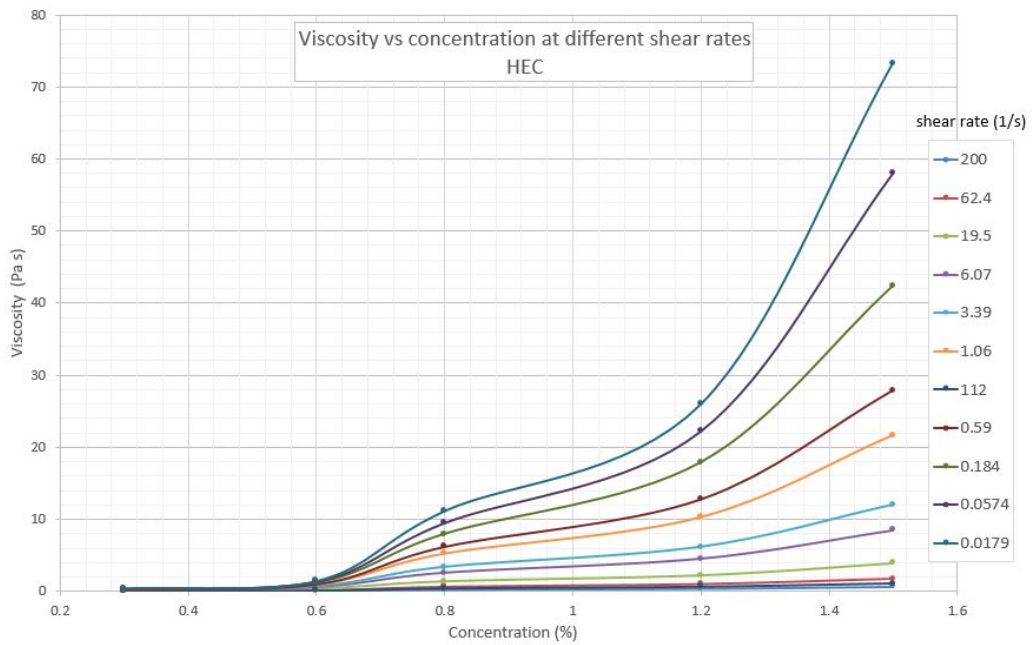

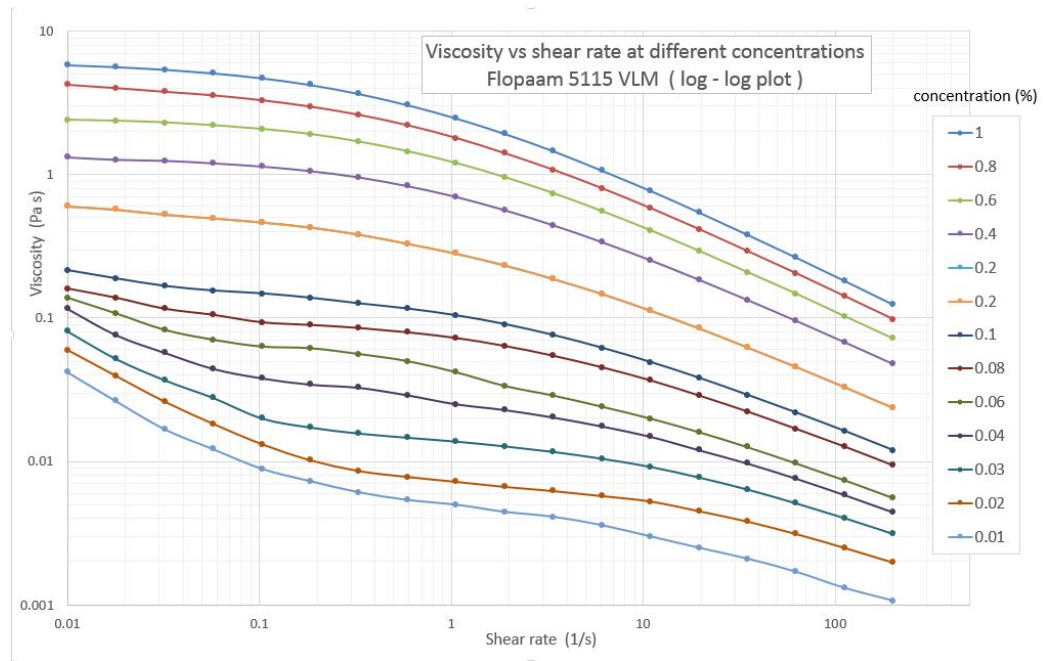Figure 36: Viscosity vs concentration at different shear rates, HEC

Figure 37: Viscosity vs shear rate at different concentrations, Flopaam 5115VLM
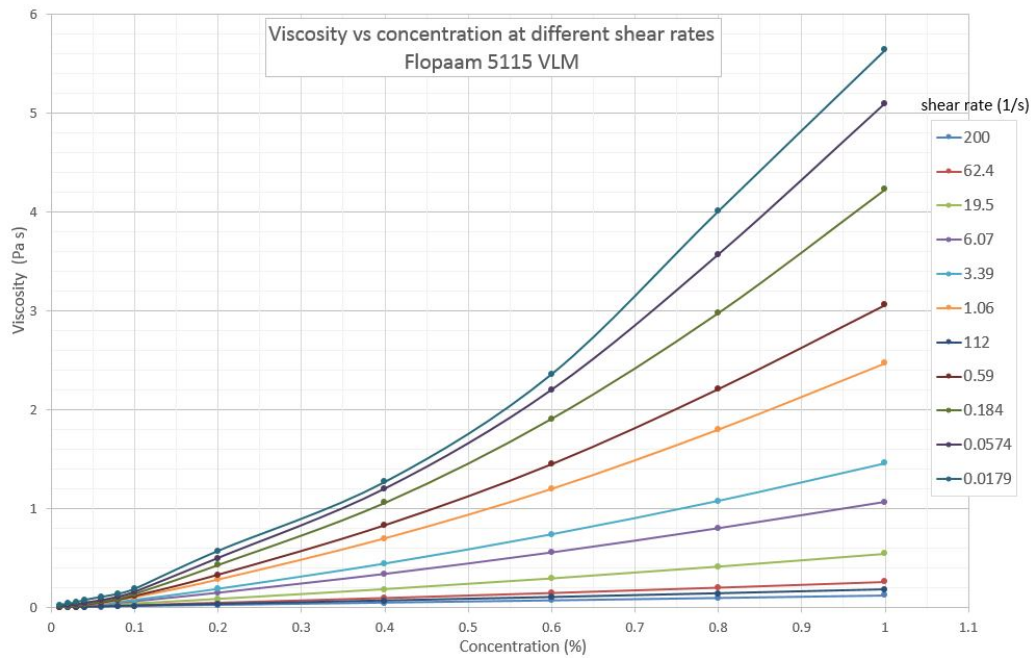

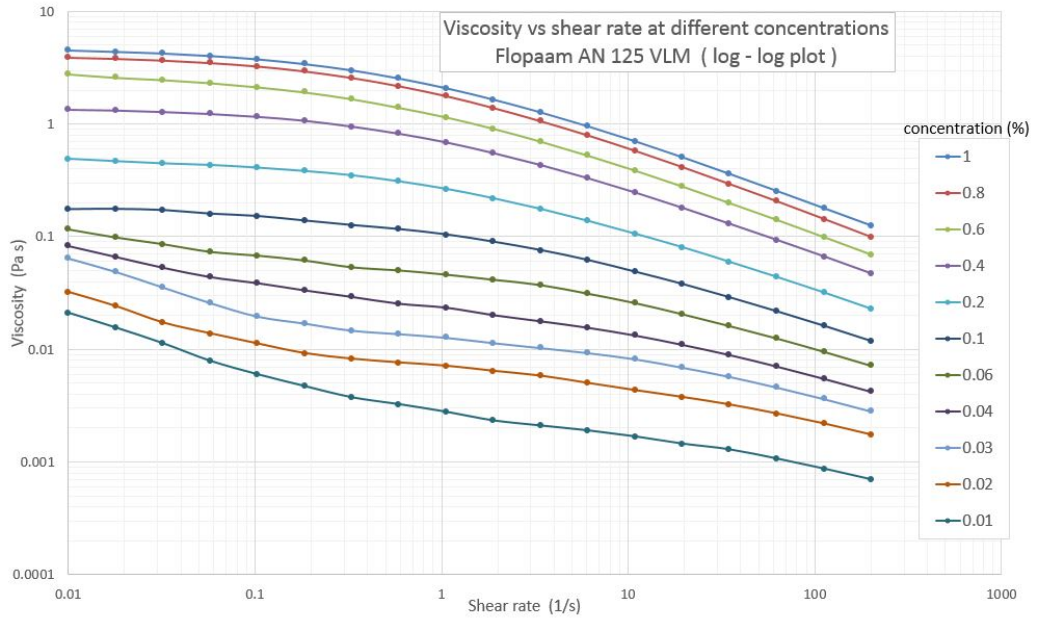Figure 38: Viscosity vs concentration at different shear rates, Flopaam 5115VLM

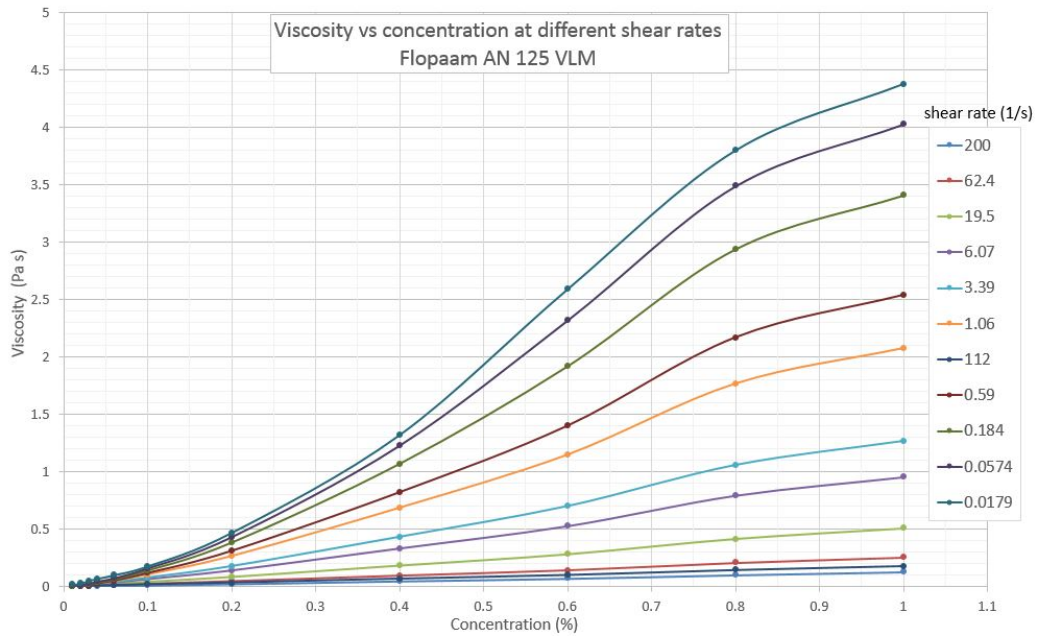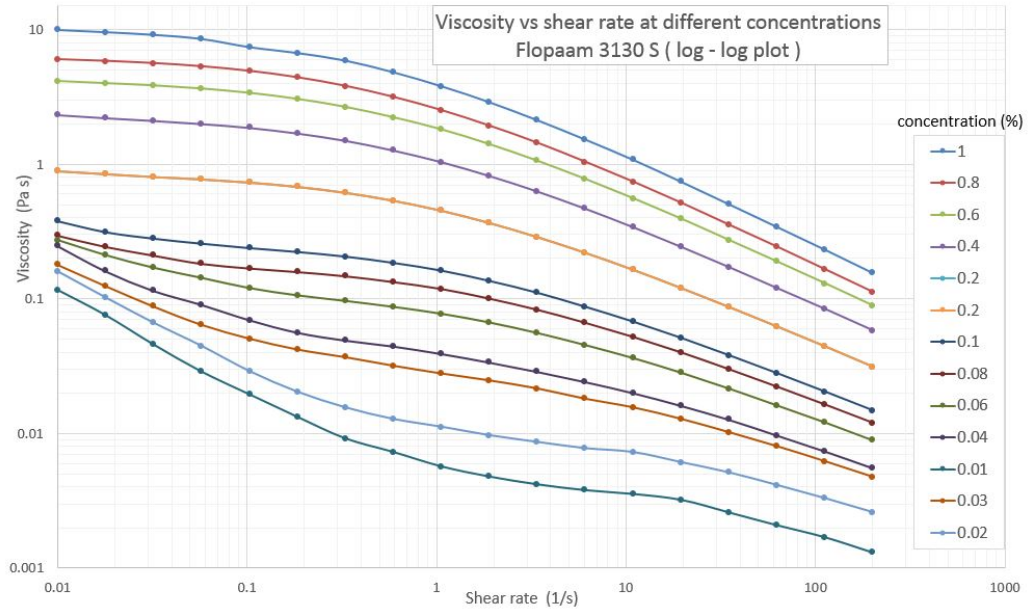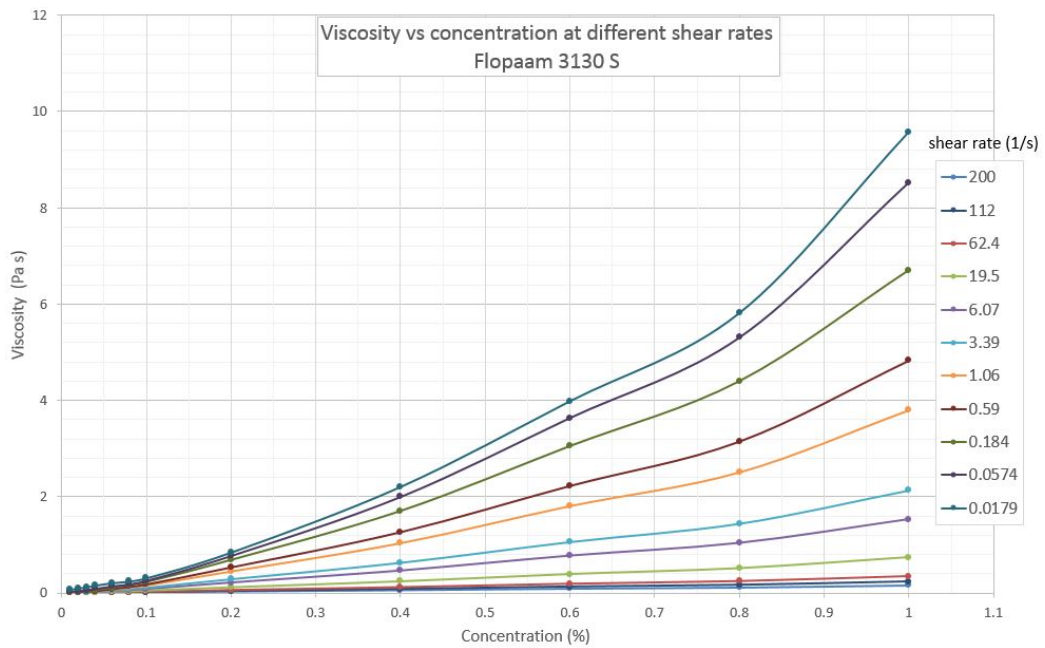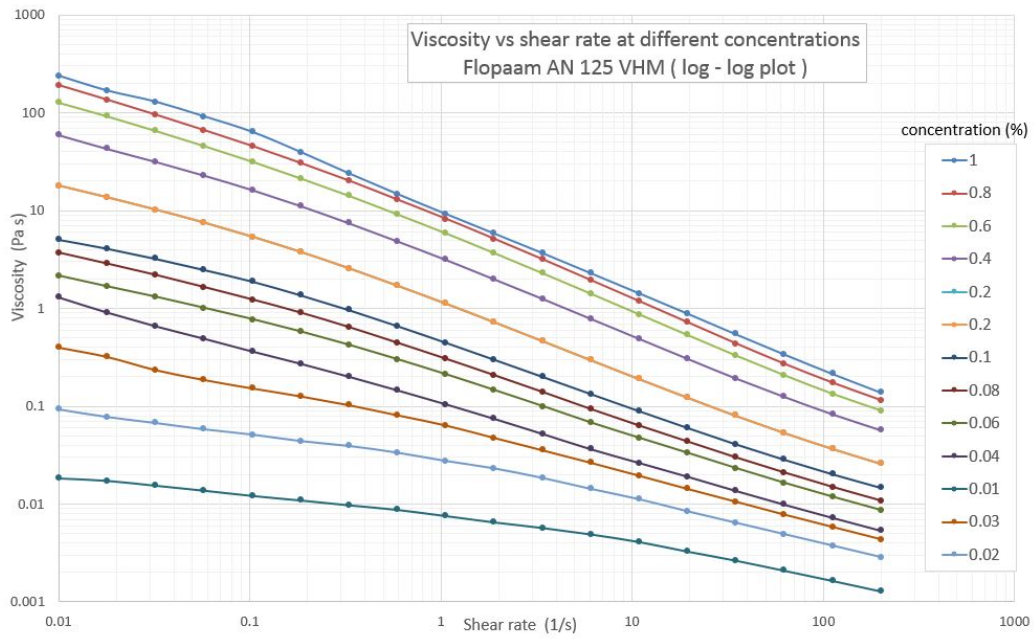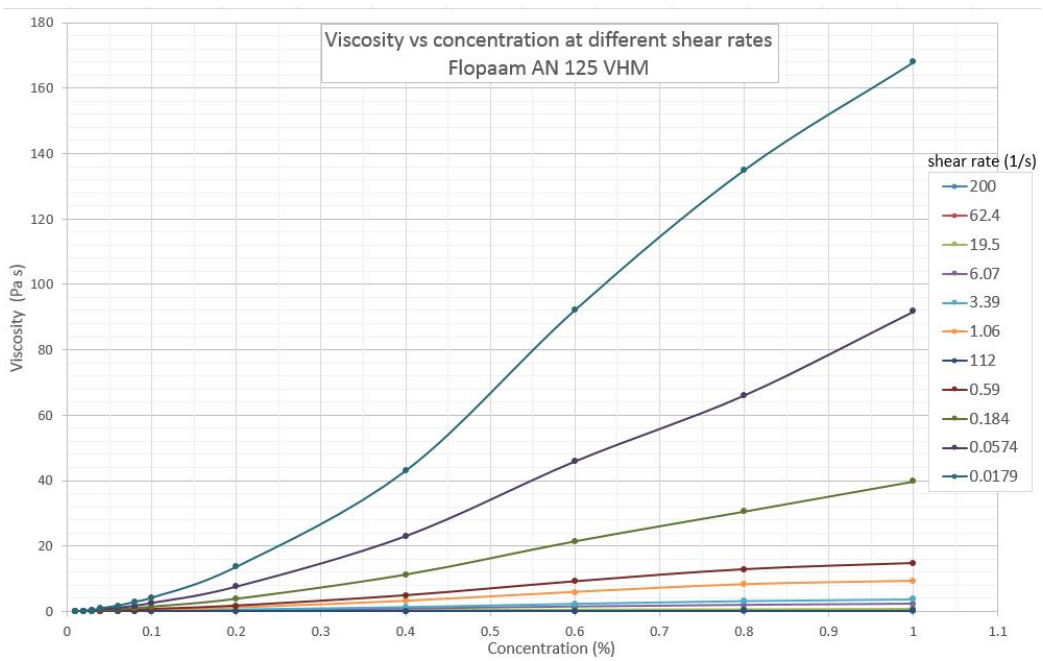Figure 39:   Viscosity vs shear rate at different concentrations, Flopaam AN125 VLM

Figure 40:   Viscosity vs concentration at different shear rates, Flopaam AN125 VLM
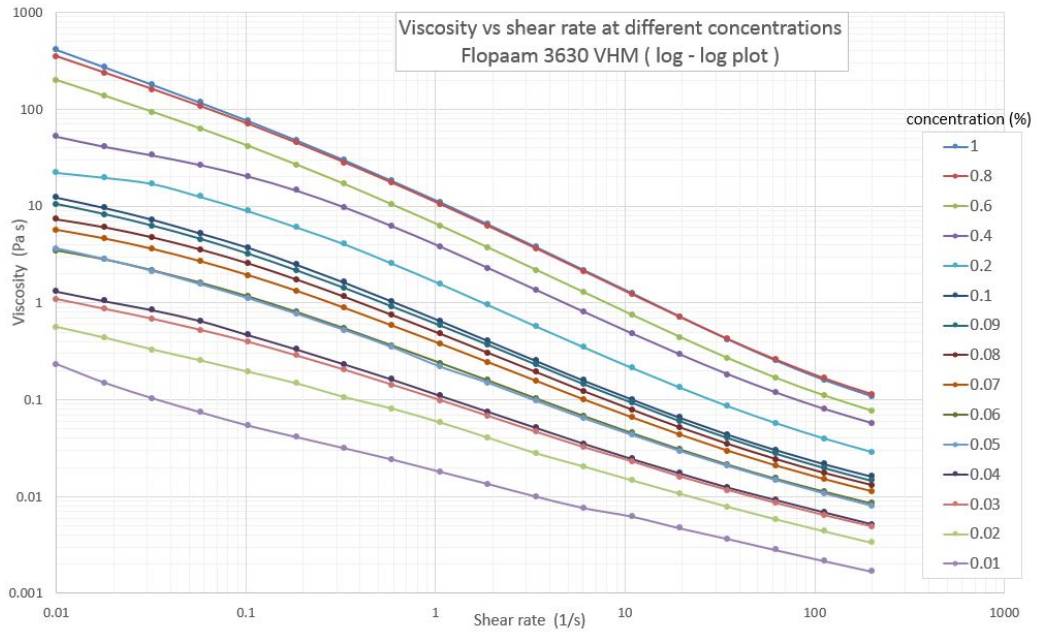
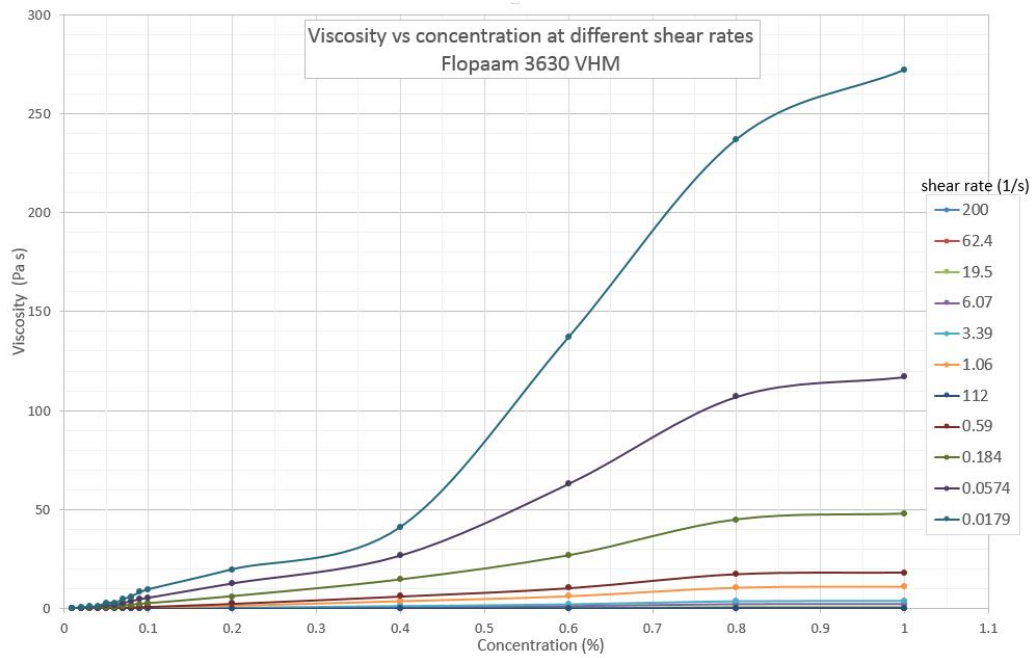Figure 41:   Viscosity vs shear rate at different concentrations, Flopaam 3130S

Figure 42:   Viscosity vs concentration at different shear rates, Flopaam 3130S

Figure 43: Viscosity vs shear rate at different concentrations, Flopaam AN125 VHM

Figure 44: Viscosity vs concentration at different shear rates, Flopaam AN125 VHM

Figure 45:   Viscosity vs shear rate at different concentrations, Flopaam 3630 VHM

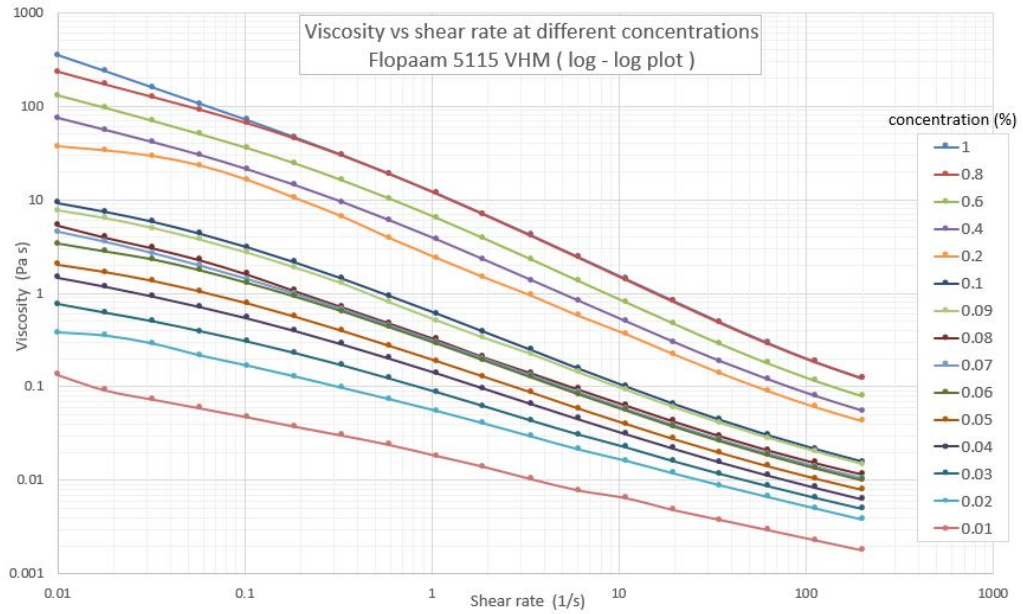Figure 46:   Viscosity vs concentration at different shear rates, Flopaam 3630 VHM

Figure 47: Viscosity vs shear rate at different concentrations, Flopaam 5115 VHM
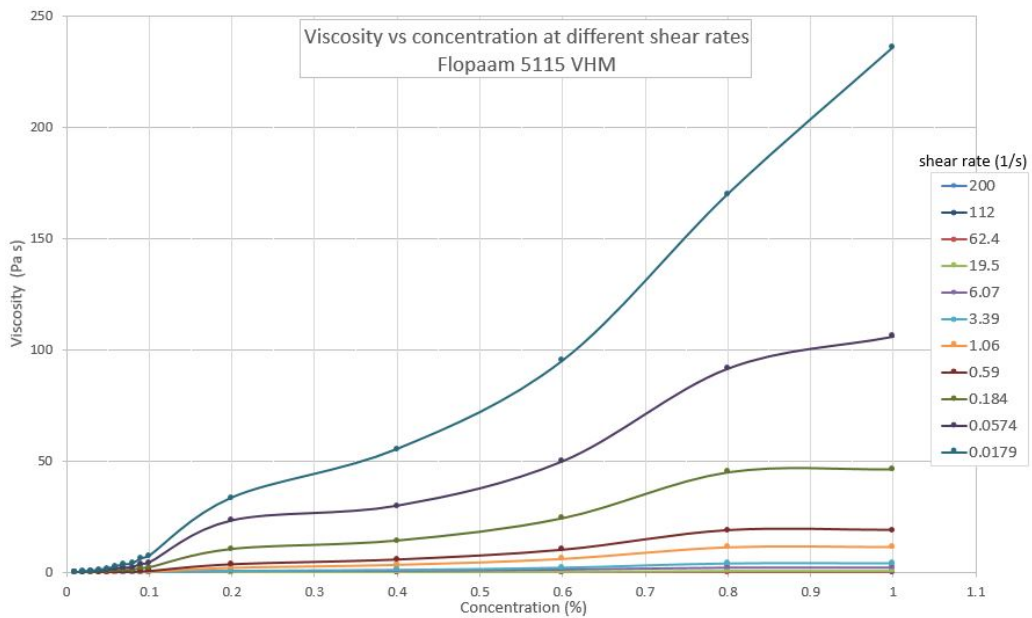

Figure 48: Viscosity vs concentration at different shear rates, Flopaam 5115 VHM

3.2   Model fitting results

For test was taken FENE-P dumbbell (further calls FENE-P) and Exponential PTT models (further calls PTT).

The experimental data was scaled in order to compare it with models.

The relation viscosity vs shear rate at different concentrations for polymer Flopaam 5115VHM is shown in Fig.50.

There are three main trends identified:

trend that present concentrations 1%-0.2% (it is lower trend on a fig)

trend that present very low concentrations 0.07%-0.05%(upper trend on a fig),

and trend with middle concentrations it might be interpreted as a transition zone.

In Fig.50 experimental data are presented as dots, while modeled curves presented by lines; FENE-P in black colour, PTT in red colour.

This plot shows good correlation of data with low concentrations and FENE-P model curve, while data with high concentrations correlates with PTT model curve. This confirms theoretical state that PPT model is designed for concentrated solutions and FENE-P for very dilute solutions (theory in Section. 1.6.4).
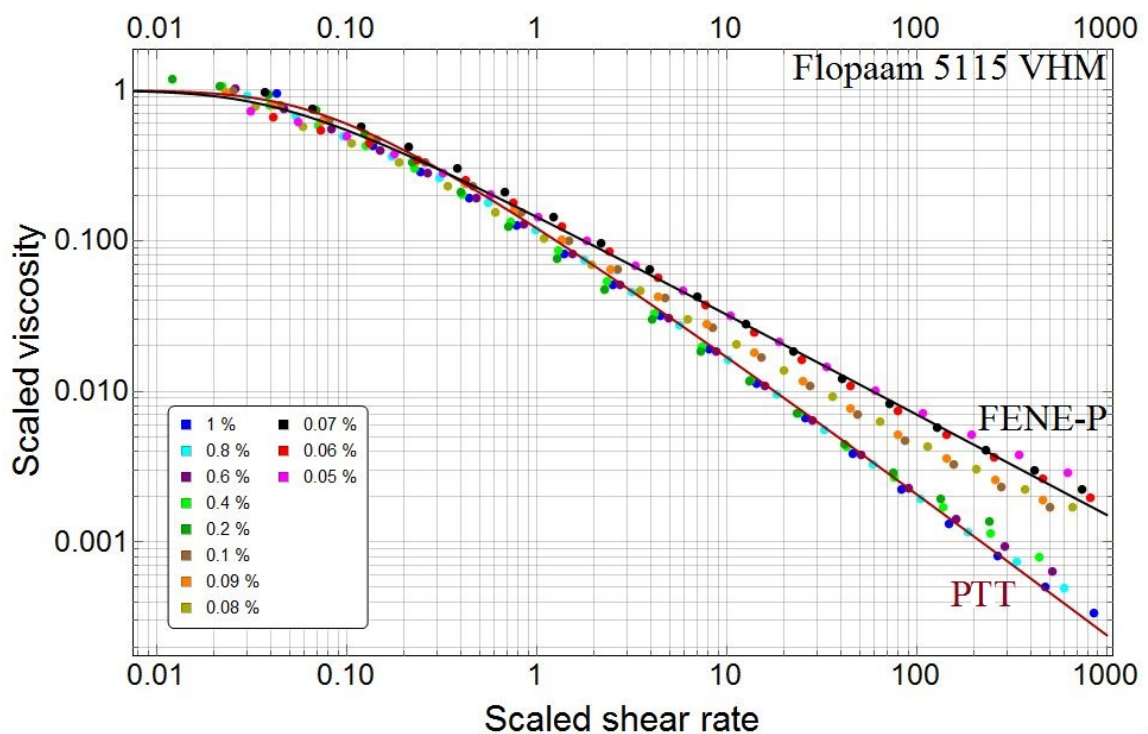

Figure 49:   scaled curves viscosity vs shear-rate at different concentrations, Flopaam 5115VHM
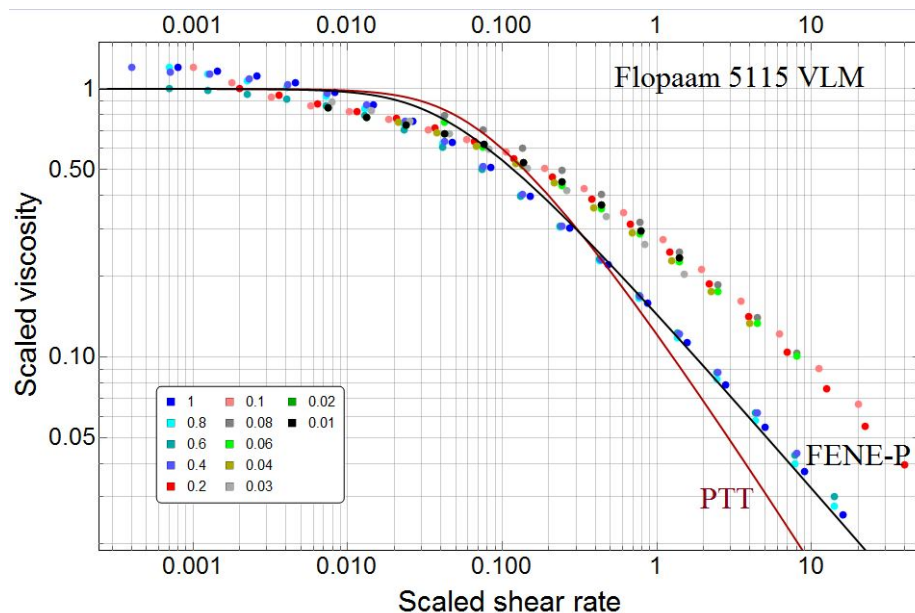
]

Figure 50: scaled curves viscosity vs shear-rate at different concentrations, Flopaam 5115VLM

Similar plot built for Flopaam 5115VLM.

There are two trends identified after scaling: trend that presented by concentrations 1%-0.4%, and all other other concentrations.

The curve from model FENE-P correlates with a high concentrations trend. Another identified trend has more gentle curve incline that does not fit curves for models. More over, this trend is higher than model curves. It also should be noted, that even though this is a polymer from acrylamide group, as well as Flopamm 5115VHM, it shows different trends. The curve from FENE-P model correlates with high concentrations Flopaam 5115VLM and low concentrations of Flopaam 5115VHM. And this confirms an idea that molecular weight has a high impact on polymer behaviour.

Next polymer to compare with model curves and with previous polymers is Flopaam 3630VHM (standard polymer group with very high molecular weight). The relation viscosity vs shear rate at different concentrations is presented in Fig. 51.

There are three trends identified:

   concentrations 1%-0.2%, correlates well with a curve for model PTT.

   trend that represented by very low concentrations 0.04%-0.03%, correlates with curve from model FENE-P.

   trend that includes data with concentrations 0.1%-0.06% is located between modeled curves.

This distribution is similar to one for Flopaam 5115 VHM , and correspond to

theoretical state that FENE-P model is designed for diluted polymers and PTT for concentrated.
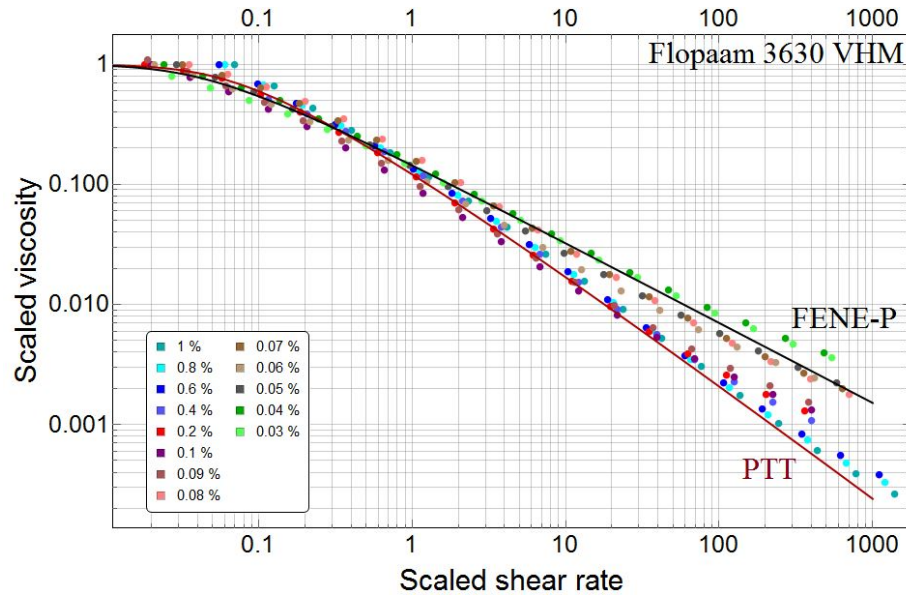

Figure 51: scaled curves viscosity vs shear-rate at different concentrations, Flopaam 3630VHM

One more polymer with very high molecular weight that is taken into comparison is Flopaam AN 125VHM.

For this polymer after scaling there are two main trends, lower trend is presented by concentrations 1%-0.4%, and it correlates with model curve PTT , another trend is represented by concentrations 0.1%-0.06% and it correlates with a model curve FENE-P. The data presented by very low concentrations have very small angle of slope, located above all presented trends and do not follow any modeled curve.
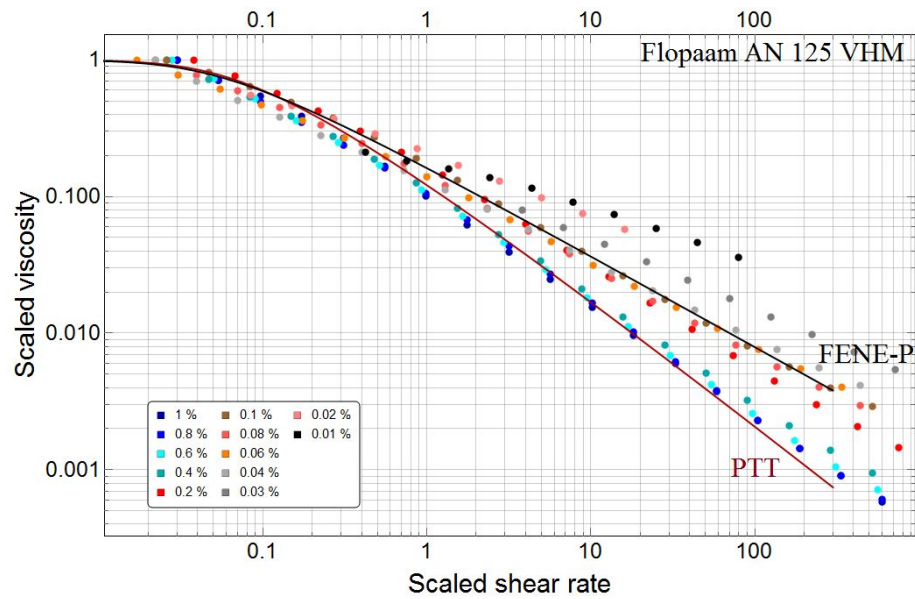
Figure 52: scaled curves viscosity vs shear-rate at different concentrations, Flopaam AN125VHM

Even though we can say about correlation with model curves, the concentrations matching models are different than in a case with Flopaam 5115VHM and Flopaam 3630VHM. There is a new feature: this is a polymer with high molecular weigh, but its very dilute concentrations are much higher than models. Can it be explained only by molecular weight and concentrations? For this lets compare it with Flopaam AN 125VLM, Fig. 53.

There are two main trends identified: trend that represented by concentrations 1%-0.4%, trend that represented by concentrations 0.2%-0.1%, and a group of very dilute polymers.
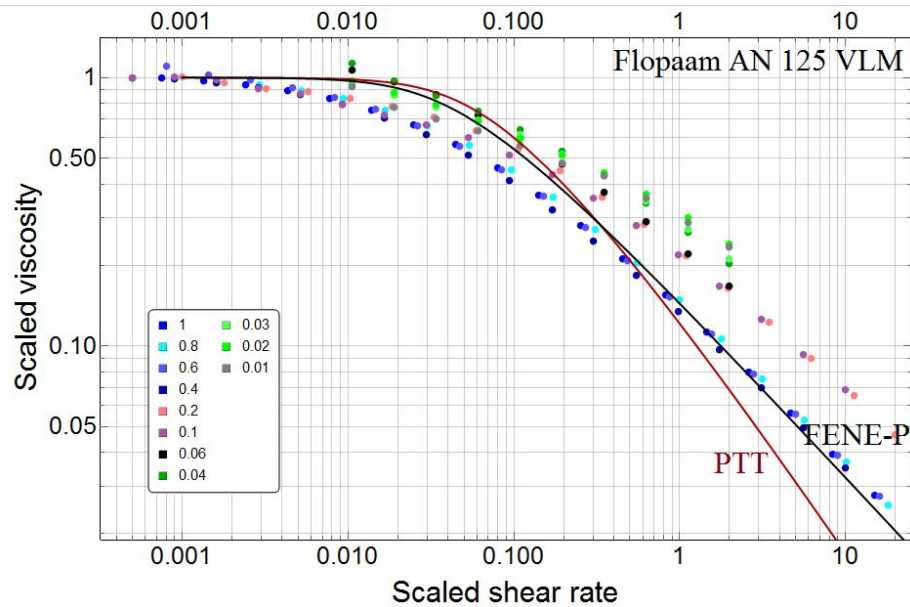
Figure 53: scaled curves viscosity vs shear-rate at different concentrations, Flopaam AN125VLM

There is no clear correlation between trends and modeled curves, however high concentrations tend can be approximated by FENE-P curve, while very dilute solutions have a very small angle of slope that does not correlate with modeled curves.

A very similar behaviour was observed for Flopaam 5115VLM, that is also polymer with very low molecular weigh. Both these polymers have trend in concentrations 1%-0.4%, that correlates with FENE-P model curve, and in both cases lower concentrations presented by trend with a very small angle of slope, which does not correlates with tested models.

In Flopaam group there is one more polymer Flopaam 3130S Fig.54 with "ultra" low molecular weigh and it will finalise model fitting for Flopaam group.

There are two main trends, and one of them can be defined by FENE-P model. This polymer, as well as polymers Flopaam 5115VLM and AN 125VLM shows correlation with FENE-P model at concentrations 1%-0.4%, and more diluted concentrations located above this trend.
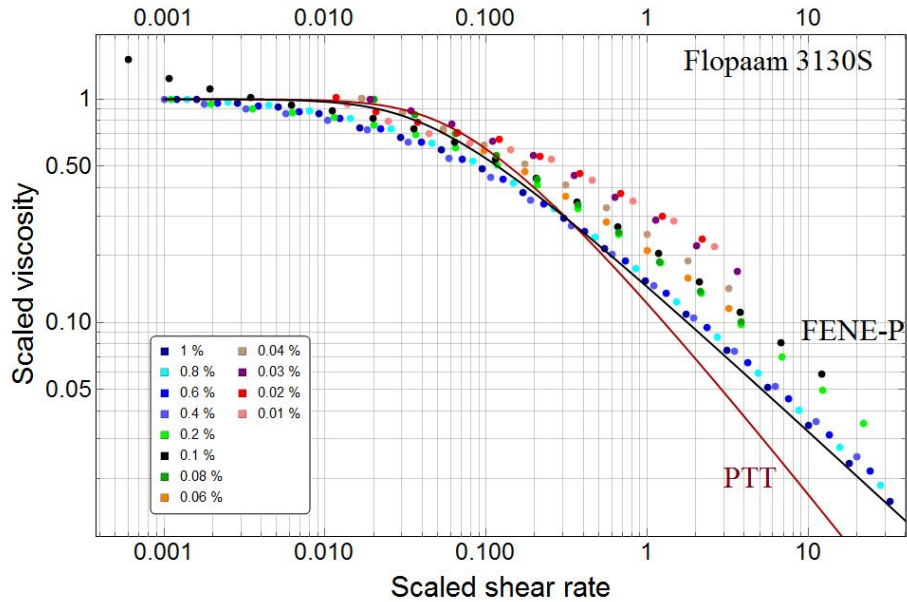
Figure 54: scaled curves viscosity vs shear-rate at concentrations 1%-0.4%, Flopaam 3130

To have a complete overview of polymers used in this work, here presented two more plots with different concentrations for HEC , Fig.55 and Xanthan, Fig. 56.

For HEC can be identified one trend for all concentrations 1.5%-0.6%, and it correlates with model curve FENE-P.

There are two trends: one is presented by concentrations 1%-0.6%, and this trend is very close to the model curve FENE-P, other concentrations located above this trend and have less steep slope.
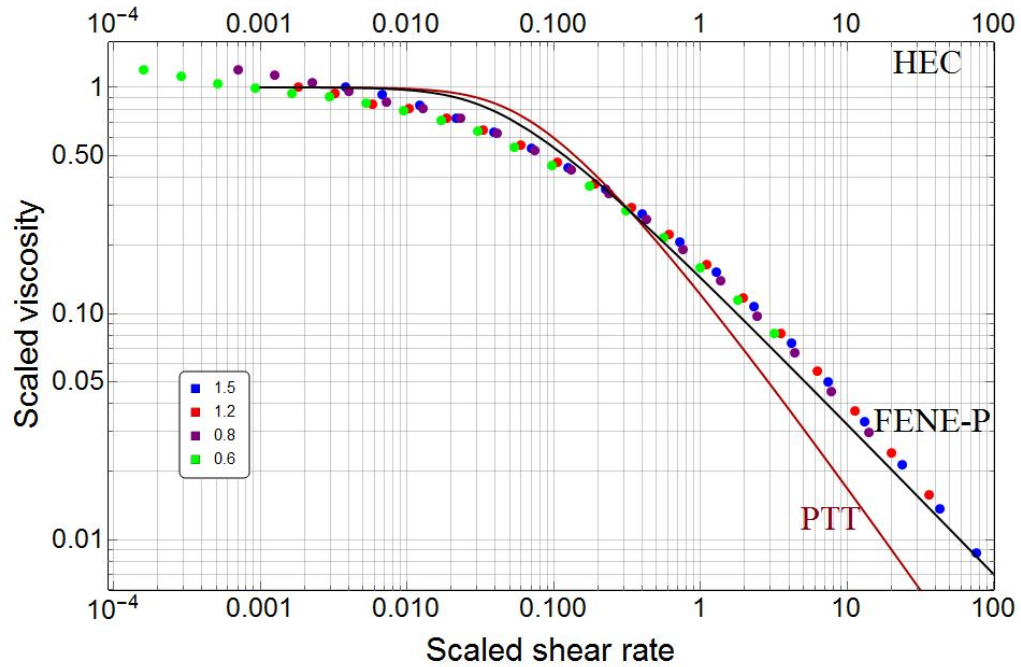
Figure 55: scaled curves viscosity vs shear-rate at different concentrations, HEC
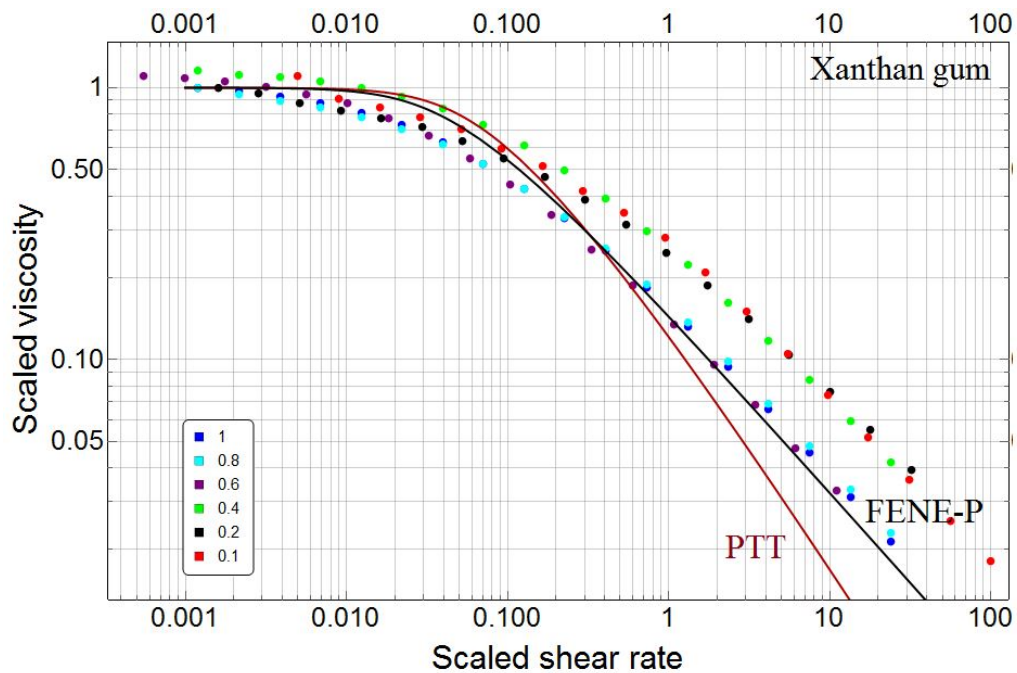

Figure 56: scaled curves viscosity vs shear-rate at different concentrations, Xanthan

In summary:

It was observed separation into three trends for polymers **Flopaam 5115 VHM** and **Flopaam 3630 VHM**. For both polymers there is a clear trend at high concentrations 1%-0.2%, and this trend is correlates with model curve PTT. Also, for both polymers seen a trend at low concentrations, in a range 0.06%-0.03% it correlates with model curve FENE-P. For both polymers there is one more trend located between PTT and FENE-P curves.

For polymers **Flopaam 5115 VLM** , **Flopaam AN 125 VLM** , **Flopaam AN 125 VHM** and **Xanthan gum** there are two main trends is observed. There is a trend at concentrations 1%-0.4% for Flopaams and 1%-0.6% for Xanthan; which correlates with model curve FENE-P. Data with lower concentrations located above the model curve FENE-P. For these plots is also noted, that data with low concentrations have less inclined slope that our model curves, and they can not be fitted into model by scaling methods.

Analysis of plots with HEC showed main trend for concentrations 1.5%-0.6% and this trend correlates with FENE-P curve. As theory state FENE-P model should be used for very dilute polymers, and it is known that HEC has very low molecular weight. Our test proved that HEC can be considered as a very dilute polymer even at relatively high concentrations.

Conclusion :

Experiments showed some similarity in according to concentrations and some similarity in according to molecular weigh. There were three Flopaams with a very high molecular weight and two of them showed three trends, two of these trends match model curve.

Flopaams with very low molecular weight also have similarity in a way that their high concentration can be described by FENE-P model, but low concentrations need additional model.

Another similarity for all tested polymers is a trend for mid concentrations. This trend was clear for group of Flopamms with very high molecular weight, and with some approximation it can be identified for Flopamms with low molecular weight. But this trend does not fit model curve, so there is a need in a model that can describe transit concentrations.

Experiments proved that there is no one universal model that can be applied to all polymers. There are different models should be used, even for one polymer, to describe high, low and mid concentrations. This means that any flow prediction should starts with laboratory test to identify which model can be applied.

4   Conclusions

In the beginning of this work a question what is a "very dilute" solution was asked, and experiments gave the answer. The linear trend at low concentrations was identified during analysis of graphs with different polymers. For Flopaam group a concentration below which all other concentrations can be considered as very dilute was identified as 1 000ppm; for HEC it starts below 6 000ppm; for Xanthan 4 000ppm.

It means that there is no one unique number. Different polymers have different range of concentrations that can be called very dilute. From this follows, that tests should be run for each used polymer to identify region with very dilute concentrations.

We need to distinguish where is a low and where is a high concentration due to there are different mathematical models used to describe their flow. In this work were tested two models: FENE-P dumbbell and exponential PTT. From theory is known that FENE-P model designed for very dilute solutions and PTT for high concentrations. For polymers Flopaam 5115VHM and 3630VHM this theoretical state confirms perfectly. The concentrations $1 - 0.2$ have a good match with model curve PTT; concentrations $0.05 - 0.03$ have a good match with model curve FENE-P, and both these polymers have a trend in a middle which does not match any model curve. Polymer solutions with lower molecular weight also can have three trends, and in most cases the highest concentration will match with FENE-P model. From this follows, that even that theory state that FENE-P model is designed for low concentrations each polymer has its own low concentration, and therefore must be tested before model is applied to it.

Also there was identified a trend between low and high, and this trend can not be fitted into model curve by scaling. There is a need in additional model.

The polymers with low molecular weigh at low concentrations showed very flat trends which can not be fitted to model curves, by scaling, due to a very small angle of their slope. Such trends needs to be understood. It might be that these concentrations are extremely low and we did not reach concentration that will fit FENE-P, if so, then to reach model curve should be increased concentration or derived a new model.

It should be remembered that measuring non-Newtonian viscosity alone does not provide a complete description of a polymers rheology and does not allow to predict its behaviour in complex flows. While this work is concentrated on the viscosity function, another material functions need to be used for model testing.

Bibliography

Weissenberg, K. (Mar. 1947). "A continuum theory of rheological phenomena." In: *Nature* 159, p. 310.

Bird, R. B. (1977). *Dynamics of polymeric liquids.* Vol. 1. John Wiley and Sons, Inc.

Thien, N. P. and R. I. Tanner (1977). "A new constitutive equation derived from network theory". In: *Non-Newtonian fluid dynamics* 2, pp. 353, 365.

Bird, B. B., C. F. Curtiss, and R. C. Armstrong (1987). *Dynamics of polymeric liquids. Kinetic Theory.* Second edition. Vol. 2.

Bartenev, G. and S. Frenkel (1990). *Fizika polimerov.* Leningrad Khemistry.

Anderson, John David (1995). *Computational Fluid Dynamics:basics with applications.* Ed. by John J. Corrigan and Eleanor Castellano. McGraw-Hill, Inc.

Heel, A. P. G. van, M. A. Hulsen, and B. H. A. A. van den Brule (1997). "On the selection of parameters in the FENE-P model". In: *non-Newtonian fluid mechanics* 75, pp. 253, 271.

Garsia-Ochoa, F. et al. (2000). "Xanthan gum: production, recovery and properties". In: *Biotechnology advances* 18, pp. 549, 579.

Heel, Van (2000). "Simulation of viscometric fluids". PhD thesis. Technical University Delf.

D.Shogin (20018). "Fluid dynamics, lecture notes."

Teraoka, Iwao (2002). *Polymer solutions.* Vol. An introduction to physical properties. John Wiley and Sons, Inc.

V.U.Topolov (2002). *Metodicheskie ukazaniya.* Vektory i tenzory v kurse fiziki. Rostov na Donu.

Jan, F., M. Cook, and M. Graham (2008). *Hydrocarbon exploration and production.* Vol. 55. Elsevier Science.

Zuev, V., M. Uspenskaya, and A. Olehanovich (2010). *Physics and chemistry of polymers.* Information technologies in Mechanics and Optics, StPeterburg State University. StPeterburg.

Wever, D. A. Z., F. Picchioni, and A. A. Broekhuis (Nov. 2011). "Polymers for enhanced oil recovery: a paradigm for structure-property relationship in aqueous solution". In: *Progress in polymer science*, pp. 1558, 1628.

Shaw, Montgomery T. (2012). *Introduction to polymer rheology.* A John Willey and sons, INC.

SNFFloergel (Sept. 2012). *Enhancing polymer flooding performance. 30 years of experience in enhanced oil recovery.*

Floerger, SNF (2015). *EOR 101 Petroleum geology and Petroleum systems.*

Mezger, T. G. (2015). *Applied rheology.* Anton Paar GmbH.

Shogin, D., P. A. Amundsen, and A. Hiorth (2017). "Rheology of polymeric flows in circular pipes, slits and capillary bundles: analytical solutions from kinetic theory". In: *IORNorway2017 19th European symposium on IOR.*

NPD (2018). *http://www.npd.no/en/Topics/Improved-Recovery/Temaartikler/Positive-prospects-for-producing-more/.*