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Abstract

Polymer solutions are non-Newtonian fluids used in enhanced oil recovery due to their specific properties: Adding high-molecular-weight polymers to injected water significantly increases the apparent viscosity of the latter, which leads to improved sweep efficiency and allows to recover more oil from a reservoir.

Under certain flow conditions, polymer molecules can undergo mechanical degradation: rupture of polymer chains under large stresses. This effect is undesirable, since the polymer solution gradually loses its important properties when it degrades.

Although the impact of degradation on shear viscosity is well understood from experiments, it is not clear how degradation affects the polymer behavior in complex flows, when non-trivial geometries and time - dependent effects are involved.

The first step to understanding of the role of mechanical degradation can play in complex flows is realizing how it affects different material functions,describing the polymer dynamics at various flow regimes. To do that, use of the differential tensor FENE-P Bead-Spring-Chain model of polymeric liquids, based on kinetic theory plays important role. In this model,each polymer molecule is represented by a very long linear chain consisting of identical spherical beads connected by non linear springs. Mechanical degradation i.e.rupture of polymeric chains, can therefore be described by a simultaneous change in bead number and number density of polymer molecules. For this a simple degradation scheme is considered which is gradual erosion from the ends. The material functions for FENE-P Bead-Spring-Chain model are derived and scaled plots, through which the impact of degradation on the material functions including viscosity can be studied, are made.

Nomenclature

Bsc	bead - spring - chain
DB	Dumbbell
EOR	Enhanced oil recovery
FNSD	First normal stress difference
IOR	Improved Oil Recovery
NSC	Norwegian Continental Shelf
SNSD	Second normal stress difference
ρ	Density of fluid
T	Temperature
v	velocity of fluid
V	arbitrary volume
∇	nabla
π	Total stress tensor
δ	Unit tensor
τ	Anisotropic stress tensor
p	Thermodynamic pressure
n	the number concentration
κ	second or bulk or dilational viscosity
$\dot{\gamma}$	rate of strain tensor
$\dot{\epsilon}$	elongation rate
η_0	viscosity at zero shear rate
η_∞	viscosity at infinite shear rate
ψ_1	first normal stress difference
ψ_2	second normal stress difference
η' and η''	complex viscosity coefficients.
ψ'_1 and ψ''_1	complex first normal stress differences
ψ_1^d	First normal stress displacement coefficient
λ	time constant
ζ	frictional coefficient
N	number of beads in the polymeric chain

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Introduction

Polymers are widely used in the world to recover the oil. One of the most promising method which is using polymers to recover the oil is Enhanced oil Recovery(EOR). According to Norwegian Petroleum Directorate,the most promising method of Enhanced oil recovery(EOR) on the Norwegian continental shelf (NCS) is polymer combined with low salinity flooding for enhanced EOR.[Directorate, 2017] The essence of this method is adding high molecular weight polymer to the injected water. This process significantly increases the apparent viscosity of water,which leads to improved sweep efficiency and enables to recover more oil from reservoir.

Polymer solutions contain macro-molecules and possess their specific properties.The fluids which obey classical laws i.e.Newton's laws are called Newtonian fluids for example oil, water etc. and the liquids which do not obey these laws are Non- Newtonian. Macro molecular fluids do not obey these laws and hence they are Non- Newtonian. By solving the equations of fluid dynamics namely Navier-Stokes equations[Bird et al., 1987a],motion of any fluid can be described. The most important physical quantity in this equation is 'stress tensor' which clearly visualizes how the forces are distributed in the fluid . In case of Newtonian fluid, stress tensor has straightforward form and can be calculated if the viscosity of fluid is provided.But, in case of Non- Newtonian, it is not easy to calculate the stress tensor. It can be obtained from constitutive equation which in turn must be derived by means of non-equilibrium thermodynamics [Bird et al., 1987a]

Most of the industrial problems deals with simple shearing flow.In such flows,one of the most important characteristics considered is Non-Newtonian viscosity . Many correlations with this quantity has been proposed and employed more or less effectively. The model proposed with this correlation are able to describe steady state flows in very simple geometries. But In the reservoir, the polymeric liquid flows through the porous rock which is an example of complex geometry and the flow is commonly time dependent.

To describe simple shear flow there are many mathematical and physical models. When the fluid flow is time - dependent and complex it may not be easy to understand everything with the help of correlation only. In addition in complex flow, molecules of polymers may be degraded. When the polymeric fluid is subjected to very large shear stress, the chain of polymer molecules breaks and this phenomena is called mechanical degradation.

The problem of degradation is very important to study the non - Newtonian fluid phenomena.As the polymeric chain breaks,the chain of polymer molecules becomes shorter, as a result viscosity

decreases. This is undesirable in EOR.

Even advanced polymer models are also not able to describe the degradation. So my works here will be focused on developing a framework for describing mechanical degradation of polymer molecules using FENE-P bead - spring - chain model.

Objective of Study

This study is focused to develop a differential tensor Non-Newtonian fluid model supporting mechanism of polymeric chains [Caruso et al., 2009] to describe the mechanical degradation of polymers. Polymer fluid dynamics in simple flows can be described in terms of "material function". The first step to understand the impact of mechanical degradation on complex polymer flows is realizing how degradation affects these material functions. For this, FENE-P Bead-Spring-Chain model of polymeric liquid based on kinetic theory is used

1 Fluid Dynamics

Simply liquids and gases are called fluid. The motion of any fluid is described by the equations of conservation of mass, momentum and energy. [Bird et al., 1987a]. To derive these equations, following assumptions are made.

Fluid is a continuous medium which means scalars such as temperature, T , and density, ρ , are defined at each point of fluid. The velocity field of fluid, \mathbf{v} , is in space or velocity field is continuous function of space and time.

1.1 Conservation of mass

Let us assume a volume fixed in space as in the figure below. Let ds is the surface element, V is the controlled volume and \mathbf{v} is the velocity of fluid crossing the surface. Also \mathbf{n} is the unit normal vector directed outward.

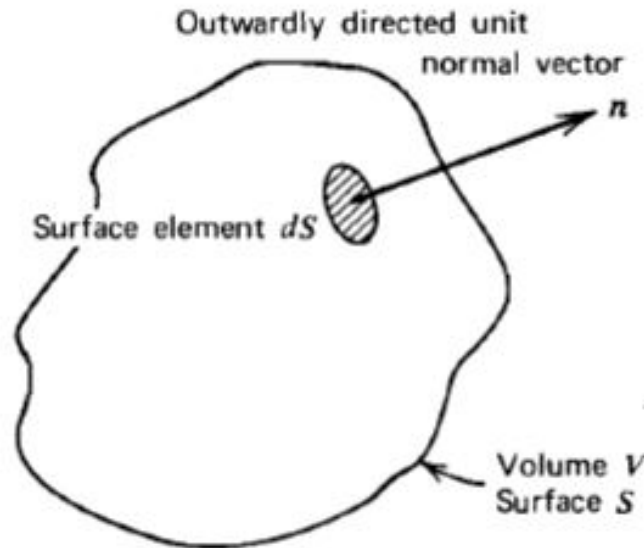


Figure 1: Control Volume Fixed in Space [Bird et al., 1987a]

where $(\mathbf{n} \cdot \mathbf{v}) dS$ is local volume flow out and $(\mathbf{n} \cdot \rho \mathbf{v}) dS$ is local mass flow rate out

It is the assumption that mass flows through the boundary then

$$\frac{d}{dt} \int_V \rho dV = - \int_S (\mathbf{n} \cdot \rho \mathbf{v}) dS \quad (1.1)$$

According to Gauss's divergence theorem, the surface integral is equal to a volume integral

$$\frac{d}{dt} \int_V \rho dV = - \int_V (\nabla \cdot \rho \mathbf{v}) dV \quad (1.2)$$

Rearranging the equation, the integral yields

$$\int_V \left[\frac{\partial \rho}{\partial t} + (\nabla \cdot \mathbf{v}) \right] dV = 0 \quad (1.3)$$

V is arbitrary, therefore

$$\frac{\partial \rho}{\partial t} + (\nabla \cdot \rho \mathbf{v}) = 0 \quad (1.4)$$

Equation (1.4) is called the equation of continuity.

For liquid, it is assumed that the density is constant. If the density (ρ), is constant, then,

$$\nabla \cdot \mathbf{v} = 0 \quad (1.5)$$

1.2 Conservation of Momentum

From figure 1,

$(\mathbf{n} \cdot \mathbf{v}) dS$ indicates local volume flow rate out and $(\mathbf{n} \cdot \mathbf{v}) \rho \mathbf{v} dS$ indicates local momentum flux out

So the local momentum flux out can be expressed as

$$(\mathbf{n} \cdot \mathbf{v}) \rho \mathbf{v} dS = [\mathbf{n} \cdot \rho \mathbf{v} \mathbf{v}] dS$$

Also, There is momentum transport by molecular process

$[\mathbf{n} \cdot \boldsymbol{\pi}] dS$ indicates local momentum flux out due to microscopic transport processes.

where, π_{ij} is the flux of positive j - momentum in positive i -direction

Now, According to principle of conservation of momentum, momentum of fluid with in v increases due to local momentum flux out which is caused by both bulk and molecular flow and external gravitational force.

$$\frac{d}{dt} \int_V \rho \mathbf{v} dV = - \int_S [\mathbf{n} \cdot \rho \mathbf{v} \mathbf{v}] dS - \int_S [\mathbf{n} \cdot \boldsymbol{\pi}] dS + \int_V \rho \mathbf{g} dV \quad (1.6)$$

where \mathbf{g} represent the force per unit mass due to gravity. According to Gauss's divergence theorem, the surface integral in terms of volume integral can be written as

$$\frac{d}{dt} \int_V \rho \mathbf{v} dV = - \int_V [\nabla \cdot \rho \mathbf{v} \mathbf{v}] dV - \int_V [\nabla \cdot \boldsymbol{\pi}] dV + \int_V \rho \mathbf{g} dV \quad (1.7)$$

Rearranging equation (1.7)

$$\int_V \left[\frac{\partial}{\partial t}(\rho \mathbf{v}) + [\nabla \cdot \rho \mathbf{v} \mathbf{v}] + [\nabla \cdot \boldsymbol{\pi}] - \rho \mathbf{g} \right] dV = 0 \quad (1.8)$$

Since V is arbitrary, the integrated function must be identically zero Hence

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) = -[\nabla \cdot \rho \mathbf{v} \mathbf{v}] - [\nabla \cdot \boldsymbol{\pi}] + \rho \mathbf{g} \quad (1.9)$$

Equation (1.9) is the momentum equation which is Newton's second law

Alternatively, π_{ij} can be interpreted as: π_{ij} is the stress(force per unit area) acting in the positive j -direction on a surface perpendicular to the i - direction.

The total stress tensor π_{ij} can be decomposed into equilibrium and non - equilibrium parts as follow:

$$\boldsymbol{\pi} = p\boldsymbol{\delta} + \boldsymbol{\tau} \quad (1.10)$$

$\boldsymbol{\tau}$ is known as the anisotropic(or deviatoric) stress tensor. It vanishes when there is no flow i.e. at equilibrium. p is the thermodynamic pressure and $\boldsymbol{\delta}$ is unit tensor. [Bird et al., 1987a] An equation that specify a value to $\boldsymbol{\tau}$ is called constitutive equation of the fluid [Bird et al., 1987a].

The constitutive equation for Newtonian fluids was established by Newton and later on it was checked experimentally and found working perfectly [Bird et al., 1987a]. So this constitutive equation is:

$$\boldsymbol{\tau} = -\mu \left[(\nabla \mathbf{v}) + (\nabla \mathbf{v})^T \right] + \left(\frac{2}{3}\mu - \kappa \right) (\nabla \cdot \mathbf{v}) \boldsymbol{\delta} \quad (1.11)$$

where μ is called coefficient of viscosity, and κ is the second, or Bulk, or dilatation viscosity.

In case of incompressible liquids, $(\nabla \cdot \mathbf{v}) = 0$ and equation (1.11) becomes

$$\boldsymbol{\tau} = -\mu \left[(\nabla \mathbf{v}) + (\nabla \mathbf{v})^T \right] = -\mu \dot{\boldsymbol{\gamma}} \quad (1.12)$$

where $\dot{\boldsymbol{\gamma}}$ is called the rate of strain tensor. From equation (1.12) it can be concluded that stress tensor is linear in velocity gradient.

1.3 Newtonian fluid

Generally the fluid which follows equation (1.11) is known as the Newtonian fluid. This type of fluid consists of small molecules. Newtonian fluid follow linearity. Such type of fluid has constant viscosity and completely characterized by two material constants: density and viscosity. The viscosity is the

property of fluid by virtue of which it opposes the flow of fluid. For Newtonian fluid, the stress is given by

$$\tau_{xx} = -\mu 2\delta_x v_x. \text{ Its detail will be explained later}$$

Some examples of Newtonian fluids are: water, oil, air, alcohol, glycerin, spirit etc. Some of the graphs for Newtonian fluid are presented below in figure 2 and 3

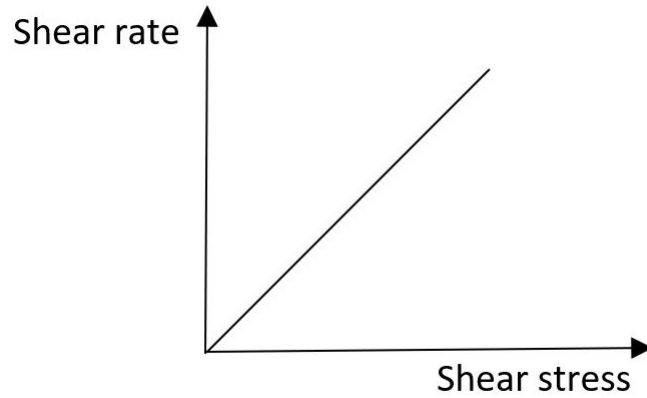


Figure 2: Relation between shear rate and shear stress for Newtonian fluid

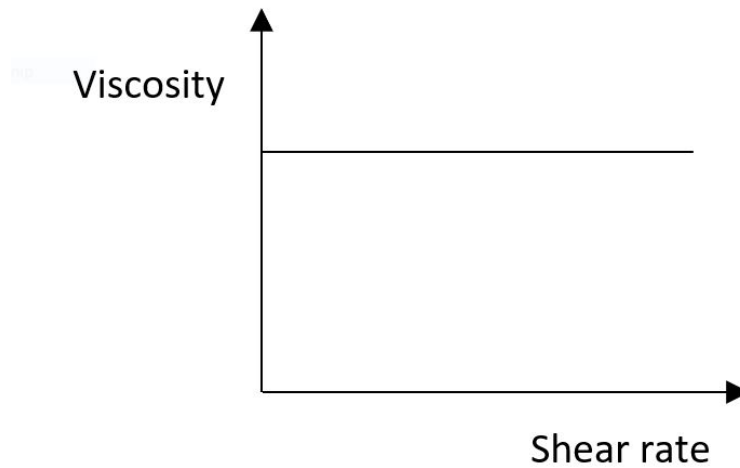


Figure 3: Relation between shear rate and viscosity for Newtonian fluid

1.4 Non-Newtonian fluid

The fluid which does not follow equation (1.11) is called Non-Newtonian fluid. This fluid consists of large molecules or contain some particles which are not spherically symmetrical. In case of this fluid, viscosity is shear dependent and hence linearity can not be observed. To describe this fluid, more than two parameters are required which are called 'material functions'. The parameters which describe this fluid are: shear rate, time, frequency, pressure etc. Some examples of Non-Newtonian fluids are: polymer solution and its melts, blood, lymph, mucus, micellar water, ketchup, fish soup, drilling mud etc.

2 Polymers

Polymers are large molecules made up of many small simple chemical units. These small chemical units are known as structural units. In some polymers, each structural unit is connected to precisely two other structural units and the resulting chain structure is called a linear macromolecule but in the other polymers most structural units are connected to two or more than two units which are known as branched macromolecules [Bird et al., 1987a] The figure 4 below shows the symbolic representation of linear and branched macromolecules [Bird et al., 1987a]

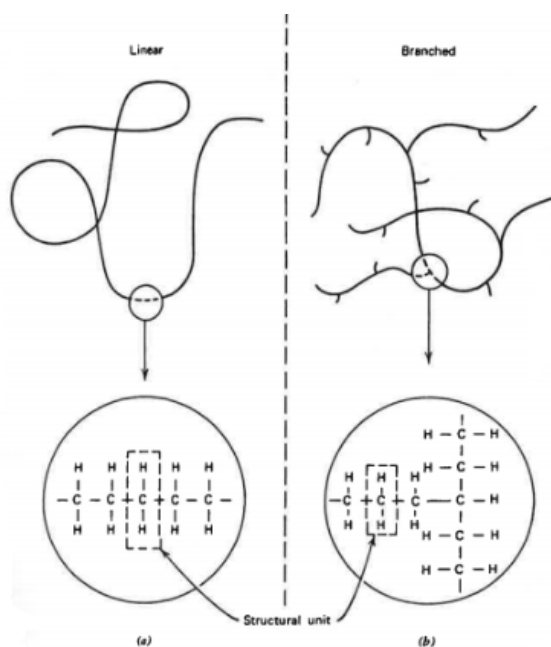


Figure 4: Symbolic representation of linear and branched macromolecules [Bird et al., 1987a]

polymers are separated in two different types which are synthetic and natural (biological). Synthetic polymers built from a single structural unit are recognized as homopolymers. Examples of homopolymers are polyethylene, polyvinylchloride and polystyrene. On the other hand, natural polymers built from two or more structural units are known as copolymers. In case of biological polymers, there are a large number of different structural units than in synthetic. Viruses, protein, DNA molecules, xanthan gum etc. are the examples of biological polymers.

The product of molecular weight of structural unit and the number of structural units in the molecule gives the molecular weight of macromolecule. A polymer sample in which molecular weight of all macromolecules is same is recognized as monodisperse but the polymer sample containing many different weights of macromolecules is referred to as polydisperse. In case of polydisperse macro-

molecular sample, the number average molecular weight can be written as

$$\bar{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \quad (2.1)$$

Where N is the number of moles of molecular weight M The weight average molecular weight can be written as

$$\bar{M}_w = \frac{\sum_i w_i M_i}{\sum_i w_i} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \quad (2.2)$$

Where $w_i = N_i M_i$

In case of monodisperse samples, these two averages are equal ($\bar{M}_n = \bar{M}_w$). and for Polydisperse samples, $\bar{M}_n < \bar{M}_w$.

The ratio

$$\frac{\bar{M}_w}{\bar{M}_n} \quad (2.3)$$

is called heterogeneity index.[Bird et al., 1987a]

2.1 Polymeric flow phenomena

Polymeric liquid shows different characteristics during the motion. Some of the observed characteristics during the motion of polymeric liquid are explained below with some experiments.

2.1.1 Non-Newtonian viscosity

One of the most important characteristic of polymeric fluid is that they are shear rate dependent or they shows Non-Newtonian viscosity. By a simple experiment as shown in figure 5, this effect can be visualized. For this experiment, two vertical identical tubes are taken and the bottom of tubes are covered by a flat plate. The two tubes are filled in such a way that one is filled with Newtonian fluid and other is filled with polymeric liquid. Initially it is assumed that both of them has same viscosity in very low shear rate. When the plate is removed and both the fluids are allowed to flow by gravity, it was observed that polymeric liquid drained faster than Newtonian. From this experiment, It can be concluded that polymer liquid has lower viscosity in high shear rate. This decrease in viscosity of liquid with increase in shear rate is known as shear thinning and the fluid is referred to be shear thinning or pseudoplastic.[Bird et al., 1987a]

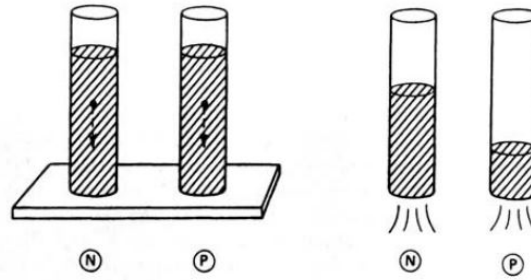


Figure 5: Tube flow and shear thinning. In each part, the Newtonian behaviour is shown on the left N; The behaviour of polymer on the right P [Bird et al., 1987a]

2.1.2 Normal stress effect

Polymeric fluid shows normal stress difference in shear flows. To understand this effect, Let us assume that a fluid is flowing along one co-ordinate direction and velocity of fluid varies in other coordinate direction. Let '1' direction represent the direction of fluid velocity, '2' direction represent the velocity variation direction and '3' direction represents the remaining neutral direction in coordinate system. [Bird et al., 1987a]

Then

$$\tau_{11} - \tau_{22} \quad (2.4)$$

gives the first normal difference.

Similarly

$$\tau_{22} - \tau_{33} \quad (2.5)$$

gives the second normal stress difference. In case of steady flow, first normal stress difference is always zero. The first normal stress of polymeric liquid is negative and always larger than the second normal stress difference. This implies that for polymeric fluid there is another extra stress in direction of streamline which is represented by the direction '1' here. [Bird et al., 1987a]

To understand the Normal stress effect, several experiments are performed. One of them is Rod climbing experiment which is demonstrated in figure 6

In this experiment, the two rotating rods are inserted into two beakers. One of the beaker is filled with Newtonian fluid and other one is filled with polymeric fluids. It is found that the Newtonian liquid near the rotating rod is pushed outward due to centrifugal force so that the dip is formed near

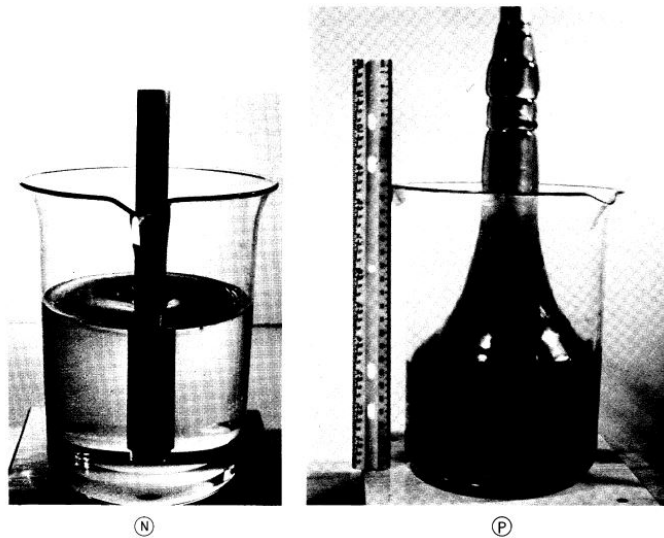


Figure 6: Rod climbing experiment. In each part, the Newtonian behaviour is shown on the left N; The behaviour of polymer on the right P. [Bird et al., 1987a]

the rod. But in polymeric liquid, polymer solution moves in opposite direction, towards the center of beaker and climbs up the rod which is shown in figure 5. [Bird et al., 1987a] [Weissenberg, 1947]

2.1.3 Elastic effect

When polymeric liquid moves, it shows elastic behavior. To visualize this effect, many experiments are performed. One of the experiments to describe this effect is the tubeless siphon as shown in figure 7

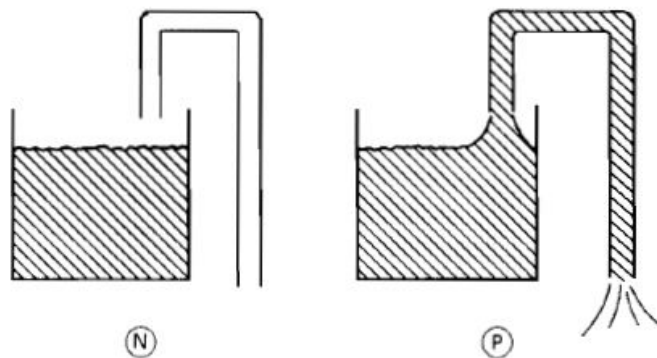


Figure 7: The Tubeless Siphon. N when the siphon tube is lifted out of the fluid, the Newtonian fluid stops flowing; P the polymeric liquid continues to be siphoned [Bird et al., 1987a]

Let us consider two identical experiment in which the fluid is siphoned out from container, First experiment using Newtonian fluid and second one is using polymeric liquid as shown in figure 7 When the tube is lifted up from Newtonian fluid, slurping sound is heard as well as fluid empties out of the tube and siphoning stops. In contrast, when the tube is lifted up from polymeric liquid, it continues to flow up and through the siphon. This is because of the elastic characteristics of polymeric liquids. [Bird et al., 1987a]

Some of the other characteristics of Non-Newtonian fluid or polymeric fluid on the basis viscosity variation with shear rate are described below:

2.1.4 Shear Thinning Behavior and Shear Thickening Behavior

If the viscosity decreases with the increase of shear rate then the process is called shear thinning. The fluid which contain components that can deform and able to rearrange to manage the flow shows this behavior and this behavior is time dependent. Examples of such fluids are blood, polymer solution and melts etc.

If the viscosity increases with the increase of shear rate then the process is called shear thickening. The fluid which contain components that can not deform or rearrange to manage the flow shows this behavior. If the flow and deformation rate increases , components become stuck and can not rearrange immediately to manage the flow due to which viscosity increases. Examples of such fluids are suspensions of titanium dioxide in a sucrose solution and corn starch in an ethylene-glycol-water mixture. [Bird et al., 1987a]

The graph of shear thinning and shear thickening behavior is as shown in figure 8

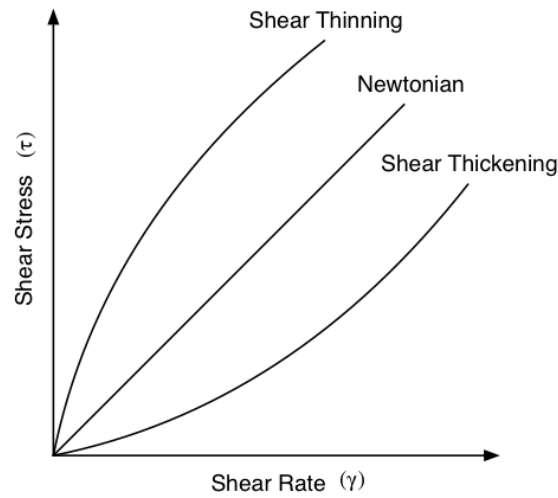


Figure 8: Shear thinning and shear thickening behaviour[Evans, 1998]

2.1.5 Bingham plastic behaviour and Viscoplastic Behaviour

Substances which are characterized by yield stress(threshold stress) are sometime called Bingham plastic For this type of fluid ,this critical shear stress must be exceeded to start flow.Example of such types of fluids are:mayonnaise,tooth paste, drilling mud etc. The Non-Newtonian fluid whose behaviour is similar to the Bingham plastic but exhibit shear thinning behaviour beyond threshold stress is called viscoplastic fluids. The graph of Bingham plastic behaviour and Viscoplastic Behaviour is as shown in figure 9.

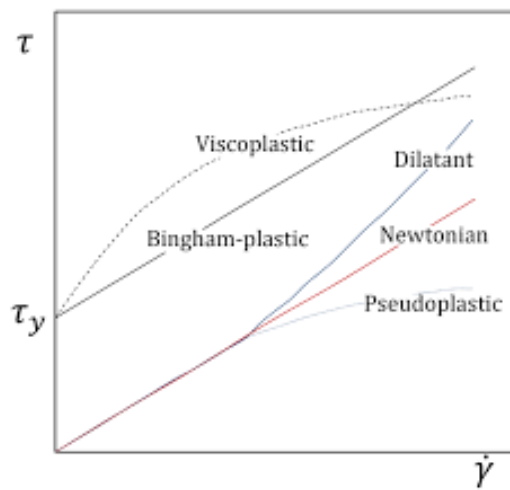


Figure 9: Bingham plastic behavior and Viscoplastic Behavior[Evans, 1998]

3 Material functions for polymeric fluids

After Several experiments performed on Newtonian fluid, it is found that there is a single material constant which is viscosity. But in case of polymeric liquid, experiments produce host of material functions that depend upon frequency, shear rate, time and so on. These material functions help to classify the fluid and hence to find the constants in Non-Newtonian constitutive equations. [Bird et al., 1987a]

To characterize the polymeric liquid, two types of flows are considered which are steady flow and unsteady flow.

3.1 Shear flow

A simple example of simple shear flow is as shown in figure 10. It consists of two parallel plates separated by a distance b and between two plates liquid is flowing in steady state. The upper plate moves with the constant velocity v_0 and here the shear rate is defined as the ratio of velocity and separation between plates which is shown in figure 10. Let the direction of fluid flow is in x -direction, velocity changes in y -direction and z -axis is neutral i.e. nothing changes along this direction.

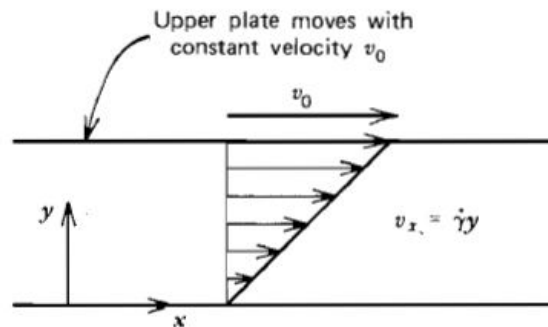


Figure 10: steady simple shear flow with shear rate $\dot{\gamma} = \frac{v_0}{b}$ [Bird et al., 1987a]

The simple shear flow is defined by the velocity field and that velocity field can be written as:

$$v_x = \dot{\gamma}_{yx}y$$

$$v_y = v_z = 0$$

where the velocity gradient $\dot{\gamma}_{yx}$ is the function of time and is called shear rate. This velocity gradient is independent of time . This type of flows are found in many polymer processing operations, for example,in many rheometer flows and in injection molding and extrusion [Bird et al., 1987a]

The next example of simple shear flow is Laminar flow which is as shown in figure 11

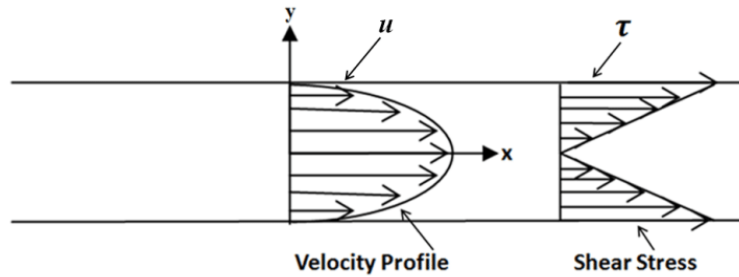


Figure 11: laminar flow in circular pipe [Mahmud, 2016]

Let 1 is the direction of flow which is "z" ,direction 2 is radial direction which is "r" and direction 3 is θ in cyclic coordinate system then velocity field for this flow can be written as

$$v = (0, 0, v_z) \text{ i.e.}$$

$$v_r = v_\theta = 0$$

3.1.1 Shearfree Flow

Shearfree flow is defined by the velocity field and that velocity field can be written as:

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

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

$$v_z = +\dot{\epsilon}z$$

where b is separation between two plates and $\dot{\epsilon}$ is the elongation rate. This $\dot{\epsilon}$ is time dependent. With the choice of values of b , different shearfree flows can be observed.

If $b = 0$ and $\dot{\epsilon} > 0$, elongational flow

$b = 0$ and $\dot{\epsilon} < 0$, biaxial stretching flow

$b = 1$, planar elongational flow.

This type of flows are found in many polymer processing operations, for example, film blowing, fiber spinning, vacuum thermoforming etc. [Bird et al., 1987a]

3.2 Stress tensor for shear and shearfree flow

The kinematics of different flows can be related by material function.

3.2.1 Stress tensors of Shear flows

It is clear that for Newtonian fluid, only the shear stress τ_{yx} remain non zero during shear flow. But in case of Non-Newtonian fluid, it is found that out of nine components four independent components of stress tensor can be non zero. So for the simple shear flow, the total stress can be written as

$$\boldsymbol{\pi} = p\boldsymbol{\delta} + \boldsymbol{\tau} = \begin{pmatrix} p + \tau_{11} & \tau_{21} & 0 \\ \tau_{21} & p + \tau_{22} & 0 \\ 0 & 0 & p + \tau_{33} \end{pmatrix}$$

where 1 represents direction of fluid flow, 2 represents the direction of velocity change and 3 is the neutral direction. There is no momentum transport in the third direction this is why only four components are sustained.

Following quantities of practical interest are introduced.

τ_{21} is called Shear Stress

$\tau_{11} - \tau_{22}$ called First Normal Stress Difference(FNSD)

$\tau_{22} - \tau_{33}$ is called Second Normal Stress Difference(SNSD)

Experimentally it is difficult to separate two quantities from $p + \tau_{11}$, so the difference is taken not the stress themselves

3.2.2 Stress tensors of Shearfree flows

The total stress tensor for shear free flows can be written as

$$\boldsymbol{\pi} = p\boldsymbol{\delta} + \boldsymbol{\tau} = \begin{pmatrix} p + \tau_{11} & 0 & 0 \\ 0 & p + \tau_{22} & 0 \\ 0 & 0 & p + \tau_{33} \end{pmatrix}$$

In case of incompressible liquid, mainly two normal stress differences are taken into account for experimental interest which are:

$$\tau_{33} - \tau_{11}$$

$$\tau_{22} - \tau_{11}$$

If we consider biaxial and elongational flow of fluid then, $b = 0$

and hence $\tau_{xx} - \tau_{yy} = 0$

So it is cleared that only single normal stress difference $\tau_{33} - \tau_{11}$ exist for this flow.

3.2.3 Material functions for steady shear flow

For Non-Newtonian fluid, the material functions for the simple shear flow are listed below:

$$\tau_{yx} = -\eta(\dot{\gamma})\dot{\gamma}_{yx}$$

$$\tau_{xx} - \tau_{yy} = -\psi_1(\dot{\gamma})\dot{\gamma}_{yx}^2$$

$$\tau_{yy} - \tau_{zz} = -\psi_2(\dot{\gamma})\dot{\gamma}_{yx}^2$$

where η is known as the non-Newtonian viscosity, ψ_1 is first normal stress coefficient and ψ_2 second normal stress coefficient. Also η , ψ_1 and ψ_2 are recognised as viscometric function. With the help of these viscometric function, one can describe only its behaviour in steady shear flow. [Bird et al., 1987a]

Experimentally found one of the well known viscometric function is viscosity. One of the experimental plot of η with shear rate are is shown bellow in figure12

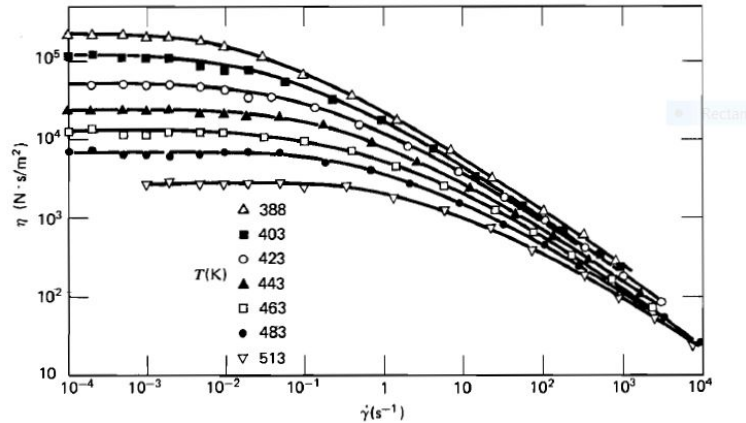


Figure 12: Non newtonian viscosity of polyethylene melt at different temperatures[Bird et al., 1987a]

In case of Non newtonian liquid, shear stress is proportional to shear rate $\dot{\gamma}$ at low shear rate and reaches to a constant value η_0 which is known as zero - shear - rate viscosity. For most of the polymeric liquid, the viscosity decreases with the increase of shear rate.

Some special behavior of ψ_1 and ψ_2 are listed below.

Behavior of FNSD

- qualitative behavior similar to $\eta(\dot{\gamma})$
- rate of decline of ψ is higher than that viscosity
- First normal stress difference is greater than zero i.e. $\psi_1 > 0$
- If the shear rate goes to zero then $\psi_1 \rightarrow \psi_{1,0}$
- If the shear rate goes to infinity then $\psi_1 \rightarrow 0$

Behavior of SNSD

- Second normal stress difference is always less than zero i.e. $\psi_2 < 0$
- The magnitude of second normal stress difference is always less than magnitude of first normal stress difference i.e. $|\psi_2| \ll |\psi_1|$ but not equal to zero eventhough it can be neglected for most fluid. [Bird et al., 1987a]

3.2.4 Material functions for unsteady shear flow

1. Small Amplitude Oscillatory Shear Flow

In this flow, it is assumed the fluid is flowing between two parallel plates and the upper plate oscillates with the frequency ω in sinusoidal oscillations. So the shear rate in time is independent of position which is given by

$$\dot{\gamma}_{yx} = \dot{\gamma}^0 \cos \omega t \quad (3.1)$$

Also,

$$\tau_{yx} = \eta'(\omega)\dot{\gamma}^0 \cos \omega t - \eta''(\omega)\dot{\gamma}^0 \sin \omega t \quad (3.2)$$

Where η' and η'' are the complex viscosity coefficients.

$$\tau_{yy} - \tau_{xx} = \psi_1^d \dot{\gamma}_0^2 - \psi_1' \dot{\gamma}_0^2 \cos 2\omega t - \psi_1'' \dot{\gamma}_0^2 \sin 2\omega t \quad (3.3)$$

where ψ_1^d is first normal stress displacement coefficient and ψ_1' , ψ_1'' are complex first normal stress difference which are functions of frequency ω .

In case of Newtonian fluid, the shear stress τ_{yx} is in the phase with shear rate $\dot{\gamma}_{yx}$. This means ($\psi_1^d = \psi_1' = \psi_1'' = 0$).

which clearly visualize that no normal stresses arise in Newtonian fluid.

For polymeric fluids, the shear stress τ_{yx} oscillates with the frequency ω without being in phase with shear rate which is shown in figure below. The normal stresses vibrate about a non zero mean value with frequency 2ω [Bird et al., 1987a]

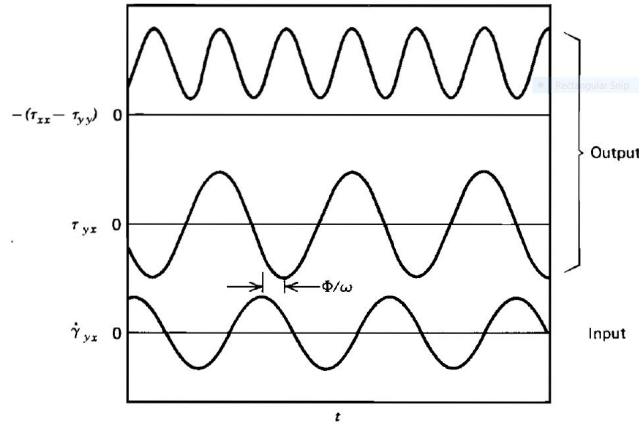


Figure 13: oscillatory shear strain, shear stress, shear rate and first normal stress difference during small shear flow [Bird et al., 1987a]

2. Stress Growth with Inception of Shear Flow

For this type experiment, fluid is considered at rest i.e. $t = 0$, this means all the stress components are zero at the beginning of flow. If $t > 0$ then $\dot{\gamma}_{xy} = \dot{\gamma}_0$. The flow is suddenly

started by applying a constant shear rate $t > 0$,so that

$$\dot{\gamma}(t) = \dot{\gamma}.H(t) \quad (3.4)$$

Where H is known as Heaviside Theta - function.

For the sudden growth of stress,the material functions are $\eta^+(\dot{\gamma}_0, t)$, $\psi^+_1(\dot{\gamma}_0, t)$, $\psi^+_2(\dot{\gamma}_0, t)$. They are defined in similar to η , ψ_1 and ψ_2 to study the momentary shear stress and normal stress difference. The meaning of plus sign of superscript belongs to a steady shear rate in positive times.Cone and plate instruments are used to measure these momentary properties. [Bird et al., 1987a]

3. Stress relaxation after Sudden Cessation of steady Shear Flow

When the steady shear flow with $\dot{\gamma}_0$ is suddenly stopped,then $\dot{\gamma} = 0$ at $t \geq 0$.

For the sudden cessation of stress,the material functions are $\eta^-(\dot{\gamma}_0, t)$, $\psi^-_1(\dot{\gamma}_0, t)$, $\psi^-_2(\dot{\gamma}_0, t)$. They are defined in similar to η , ψ_1 and ψ_2 . The meaning of negative sign of superscript belongs to a steady shear rate in negative times. [Bird et al., 1987a]

4 Generalized Newtonian Fluid Models

The fluid for which the shear stress is function of shear rate at a certain time is called Generalized Newtonian Fluid. To describe this fluid modified constitutive equations from Newtonian fluids are used. As this type of equations gives the idea of shear rate dependent viscosity, they can describe Non-newtonian viscosity of fluid. Even though these equations are not capable to describe time dependent elastic and normal stress effect. commonly used generalized fluid model is Power law model. This law is simple and sufficient to give some analytic solutions. This is why engineers use this model to get specific solutions. [Bird et al., 1987a]

4.1 Power Law Model

The shear stress τ for the Power law model can be written as [Bird et al., 1987a]

$$\tau_{12} = m\dot{\gamma}^n \quad (4.1)$$

where

m indicates the consistency, $\dot{\gamma}$ is the shear rate and n is called the power - law index.

This law can be written in the next form which is

$$\eta(\dot{\gamma}) = m\dot{\gamma}^{n-1} \quad (4.2)$$

where η indicates apparent viscosity.

If $n = 1$, $m = \mu$, the fluid is Newtonian

If $n < 1$, behavior of fluid corresponds to shear thinning

$n > 1$, behavior of fluid corresponds to shear thickening

The nature of graph for Power law model is as shown in figure 14

Some pros and cons of power la model are:

- simple, analytical solutions can be obtained.
- non - Newtonian viscosity does have a power law region.
- works nicely for flows where shear dependent viscosity is the only important non -Newtonian phenomenon.
- The limitation of this law is that it can not describe the portion of curve where $\dot{\gamma} = 0$ and $\eta = \eta_0$.

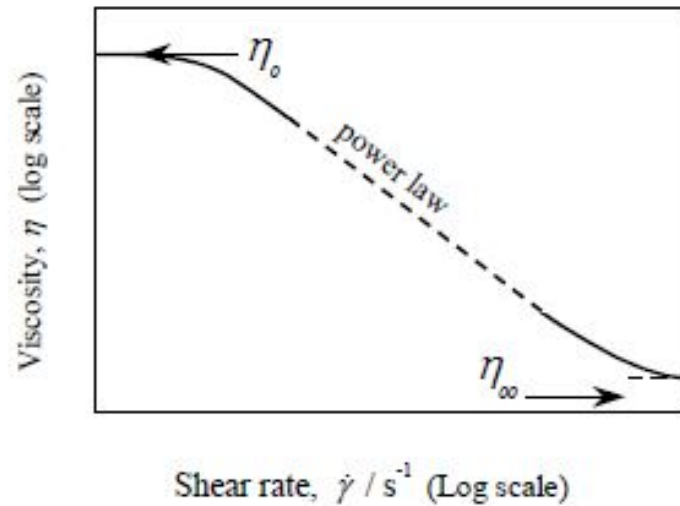


Figure 14: variation of viscosity and shear rate[Bird et al., 1987a]

4.2 Carreau-Yasuda model

There are five parameters in this model and this model is widely useful for the numerical calculation and also helps to find the analytical expression for Non newtonian viscosity. Actually this model create best curve to fit data. The expression for this model is [Bird et al., 1987a][Carreau, 1968]

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = [1 + (\lambda\dot{\gamma})^a]^{\frac{n-1}{a}} \quad (4.3)$$

where

η_0 is the zero shear rate viscosity, η_{∞} is viscosity at infinite shear rate λ is relaxation time, n is power index and a is dimensionless parameter

From the equation (4.3), it is clear that at very low shear rate ($\dot{\gamma} \ll \frac{1}{\lambda}$) and Carreau fluid act like Newtonian fluid. (At zero shear rate, $\dot{\gamma} \rightarrow 0$, $\eta \rightarrow \eta_0$) Also at very high shear rate ($\dot{\gamma} \rightarrow \infty$), $\eta \rightarrow \eta_{\infty}$, and at sufficiently large shear rates viscosity changes according to power-law ($\eta - \eta_{\infty} \sim \dot{\gamma}^{n-1}$). [Bird et al., 1987a]

The Power law model and Carreau-Yasuda model are only applicable in steady state shear flow. These models are unable to describe unsteady flow phenomena i.e. when the case of elastic response of polymeric flow need to consider, they can not explain. Also they do not predict the existence of normal stress.

4.3 Non linear viscosity constitutive equations or math models

Actually the constitutive equations are the equations of state which provide the relation between stresses and deformation variables of the fluid. Many constitutive equations are proposed to describe the time dependent flows. Some of the most effective equations are as follow:

1. **Oldroyd 8 constant model** In 1958, Oldroyd proposed this model. The empirical relation proposed by him contains quadratic form of velocity gradient and linear terms in stress tensor. This equation can give to some extent qualitatively correct results for different flows of fluid. The constitutive equation for this model is

$$\boldsymbol{\tau} + \lambda_1 \boldsymbol{\tau}_{(1)} + \frac{1}{2} \lambda_3 \{ \dot{\boldsymbol{\gamma}} \cdot \boldsymbol{\tau} + \boldsymbol{\tau} \cdot \dot{\boldsymbol{\gamma}} \} + \frac{1}{2} \lambda_5 (\text{tr} \boldsymbol{\tau}) \dot{\boldsymbol{\gamma}} + \frac{1}{2} \lambda_6 (\boldsymbol{\tau} \cdot \dot{\boldsymbol{\gamma}}) \boldsymbol{\delta} = -\eta_0 [\dot{\boldsymbol{\gamma}} + \lambda_2 \dot{\boldsymbol{\gamma}}_{(1)} + \lambda_4 \{ \dot{\boldsymbol{\gamma}} \cdot \dot{\boldsymbol{\gamma}} \} + \frac{1}{2} \lambda_7 (\dot{\boldsymbol{\gamma}} : \dot{\boldsymbol{\gamma}}) \boldsymbol{\delta}] \quad (4.4)$$

where Where $\dot{\boldsymbol{\gamma}} = \nabla \mathbf{V} + (\nabla \mathbf{V})^T$ rate of strain tensor and $\boldsymbol{\delta}$ represent the unit tensor. Also (1) represent the first contravariant time derivative . So the second order tensor $\boldsymbol{\Lambda}$ can be written as

$$\boldsymbol{\Lambda}_{(1)} = \frac{\partial \boldsymbol{\Lambda}}{\partial t} + \{ \bar{\mathbf{V}} \cdot \nabla \boldsymbol{\Lambda} \} - \{ \nabla \mathbf{V}^T \cdot \boldsymbol{\Lambda} \} - \{ \boldsymbol{\Lambda} \cdot \nabla \mathbf{V} \} \quad (4.5)$$

$\lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5, \lambda_6, \lambda_7$ and η_0 are the eight constants of this constitutive equation, where lamdas are time constants. [Bird and Wiest, 1995]

2. The Giesekus Model

This is the mathematical model with three constants ($\eta_0, \lambda_1, \alpha$) developed by Giesekus. This model is applicable to describe non linear stresses. Also this model can explain the power law region. This model is to some extent applicable to get ideas of complex viscosity and elongational viscosity. The constitutive equation is

$$\boldsymbol{\tau} + \lambda_1 \boldsymbol{\tau}_{(1)} - (\alpha \lambda_1 / \eta_0) \{ \boldsymbol{\tau} \cdot \boldsymbol{\tau} \} = \eta_0 \dot{\boldsymbol{\gamma}} \quad (4.6)$$

Where η_0 is zero shear rate viscosity, λ_1 is relaxation time and α is dimensionless mobility factor.

These mathematical models are capable to predict η' and η'' . Also they can predict the constant value of η and ψ_1 . But these model are fail to describe the other material functions of complex and time dependent flows. This is why other physical models based on the kinetic theory are required.

For the low concentration polymer solutions, kinetic theory applies and for high concentration polymer solution, network theory is used. If the concentration of solution is low, molecules can interact with solvent but in case of high concentration opposite happens. one of the model which is based network theory is The Phan-Thien-tanner Model.

3. The Phan-Thien-tanner Model

This is the model based upon network theory of polymer solutions, containing four constants. This model is derived by Phan-Thien and Tanner . It is also non linear in stresses. The constitutive equation of this model is

$$Y\boldsymbol{\tau} + \lambda\boldsymbol{\tau}_{(1)} + \frac{1}{\lambda}\varepsilon\lambda\{\dot{\boldsymbol{\gamma}} \cdot \boldsymbol{\tau} + \boldsymbol{\tau} \cdot \dot{\boldsymbol{\gamma}}\} = \eta_0\dot{\boldsymbol{\gamma}} \quad (4.7)$$

[Phan-Thien and Tanner, 1977] and [Phan-Thien, 1978] Where η_0 is zero shear rate viscosity, λ_1 is relaxation time and Y represents the function of trace of the stress tensor.

$$Y = \exp[-\varepsilon(\frac{\lambda}{\eta_0})\text{tr}\boldsymbol{\tau}] \approx 1 - \varepsilon(\frac{\lambda}{\eta_0})\text{tr}\boldsymbol{\tau} \quad (4.8)$$

The equation (4.8) holds true for small $\text{tr}\boldsymbol{\tau}$ and which makes constitutive equation simpler to use [Bird and Wiest, 1995].

5 Dumbbell Model

There are many physical models to describe the polymeric fluid flows i. e. non linear flows. One of them is Dumbbell model. This model assumes molecules of polymers as two beads of identical mass connected by an elastic spring. The spring has force constant with connector vector which is shown in figure below. This model is not enough to explain very rapid phenomena but this model is stretchable and orientable. Because of these two properties, this model can be used to describe some rheological phenomena which vary slowly with time. [Bird et al., 1987b]

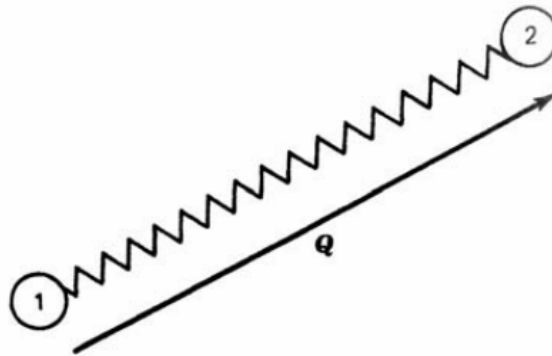


Figure 15: Elastic dumbbell connected through an elastic spring [Bird et al., 1987b]

In this model, F_c represents the connector force and Q represents the connector vector.

Some of the important assumptions made For this model are as follow:

- I) Polymer solution taken into consideration must be diluted.
- II) Solvent must be Newtonian liquid and
- III) The velocity gradient should not vary drastically at the scales of Q

Forces acting on the bead

1. Hydrodynamic drag force

when the beads moves through solvent, the experience Stokes-like force and this force is known

as hydrodynamic drag force.

2. Brownian force

Beads experience this force due to thermal fluctuations of fluid.

3. The connector force

This is the force between the beads due to connecting spring between beads. Depending upon this force there may be different types of elastic dumbbell

4. External forces

the beads may experience external forces as well. Examples of such forces are : gravitational force and electrical forces.

5.1 Kramers' Approach

The two stress tensor for dumbbell model can be written as:

$$1. \boldsymbol{\pi} = p\boldsymbol{\delta} + \boldsymbol{\tau} = p\boldsymbol{\delta} + \boldsymbol{\tau}_s + \boldsymbol{\tau}_p = \boldsymbol{\pi}_s + \boldsymbol{\pi}_p$$

where,

$\boldsymbol{\tau}_s$ represents the tensor arises due the solvent and $\boldsymbol{\tau}_p$ represents tensor arises from the polymer

$$2. \boldsymbol{\pi}_p = \boldsymbol{\pi}_p^{(c)} + \boldsymbol{\pi}_p^{(e)} + \boldsymbol{\pi}_p^{(b)}$$

Where $\boldsymbol{\pi}_p^{(c)}$ is the tensor arises due to contribution of connector , $\boldsymbol{\pi}_p^{(e)}$ gives the tensor arises due to external sources and $\boldsymbol{\pi}_p^{(b)}$ give the tensor due to contribution of beads.

Considering all the contribution and using Oldroyd derivative finally we can write

$$\boldsymbol{\tau} = -\eta_s \dot{\boldsymbol{\gamma}} - n \langle \mathbf{QF}_c \rangle + nkT \boldsymbol{\delta} \quad (5.1)$$

In equation (5.1), $\langle \mathbf{QF}_c \rangle$ is the configuration average bracket[Bird et al., 1987b]

$$\boldsymbol{\tau} = -\eta_s \dot{\boldsymbol{\gamma}} + \frac{n\zeta}{4} \langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} \quad (5.2)$$

where The Oldroyd derivative is

$$\Lambda_{(1)} = \frac{\partial \Lambda}{\partial t} + \{ \bar{\mathbf{V}} \cdot \nabla \Lambda \} - \{ \nabla \mathbf{V}^T \cdot \Lambda \} - \{ \Lambda \cdot \nabla \mathbf{V} \} \quad (5.3)$$

where ζ is called frictional coefficient and n is number density and k is Boltzman constant .The equation (5.2) represents the Kramer' form of stress tensor and equation (5.3) represents the Giesekus form of the stress tensor.

These equations(5.2) and (5.3) are

- starting points in constructing different models
- used to derive constitutive equations.
- eventually predict all the material functions.
- ultimately describe the complex flows.

5.2 Hookean dumbbell model

The Hookean dumbbell model consists of a connecting spring which is elastic or simply called Hookean. The connecting force between dumbbell can be written as $\mathbf{F}_{(e)} = H\mathbf{Q}$ [Bird et al., 1987b] where H is constant called stiffness of spring.

For this model, Kramer' and Giesekus form of stress tensors due to polymeric contribution can be written as

$$\boldsymbol{\tau}_p = -nH \langle \mathbf{Q}\mathbf{Q} \rangle + nkT\boldsymbol{\delta} \quad (5.4)$$

Kramer' form

$$\boldsymbol{\tau}_p = +\frac{n\zeta}{4} \langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} \quad (5.5)$$

Giesekus form

first our task here is to eliminate the average. So let us take the Kramer's form and multiply by $\zeta/4H$ then we get,

$$\frac{\zeta}{4H}\boldsymbol{\tau}_p = -\frac{n\zeta}{4} \langle \mathbf{Q}\mathbf{Q} \rangle + \frac{nkT}{4H}\zeta\boldsymbol{\delta} \quad (5.6)$$

Also $\lambda = \zeta/4H$. With the help of this equation(5.6) can be written as

$$\frac{n\zeta}{4} \langle \mathbf{Q}\mathbf{Q} \rangle = \lambda\boldsymbol{\tau}_p + nkT\lambda\boldsymbol{\delta} \quad (5.7)$$

Now Taking the Oldroyd derivative, we get,

$$\frac{n\zeta}{4} \langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} = -\lambda\boldsymbol{\tau}_{p(1)} + nkT\lambda\boldsymbol{\delta}_{(1)} = -\lambda\boldsymbol{\tau}_{p(1)} + nkT\lambda\dot{\boldsymbol{\gamma}} \quad (5.8)$$

With the help of equation (5.6) and (5.7) , equation (5.5) can be written as

$$\boldsymbol{\tau}_p + \lambda\boldsymbol{\tau}_{p(1)} = nkT\lambda\dot{\boldsymbol{\gamma}} \quad (5.9)$$

This is the constitutive equation of Hookean dumbbell mode.

5.3 The material functions of Hookean dumbbell model for steady shear flow

Let us assume that a fluid is flowing through two parallel plates. The velocity field for this flow can be written as:

$$\mathbf{v}_x = \dot{\gamma}y, \mathbf{v}_y = \mathbf{v}_z = 0$$

The stress tensor due to polymeric contribution is

$$\boldsymbol{\tau}_p = \begin{bmatrix} \tau_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{xy} & \tau_{yy} & \tau_{yz} \\ \tau_{xz} & \tau_{yz} & \tau_{zz} \end{bmatrix} \quad (5.10)$$

Also

$$\dot{\boldsymbol{\gamma}} = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \dot{\gamma} \quad (5.11)$$

Now

$$\boldsymbol{\nabla} \mathbf{v} = (\partial_1 \mathbf{v}_j) = \left[\frac{\partial \mathbf{v}_x}{\partial y} \equiv \partial_2 \mathbf{v}_1 \neq 0 \right] = \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \dot{\gamma} \quad (5.12)$$

The transpose of equation (5.12) can be written as

$$\boldsymbol{\nabla} \mathbf{v}^T = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \dot{\gamma} \quad (5.13)$$

$\boldsymbol{\tau}_{p(1)}$:

If there is steady shear flow, time dependent phenomena will not be observed.

$$\frac{\partial}{\partial t} = 0$$

We have,

$$\mathbf{v} \cdot \nabla = v_x \partial_x + v_y \partial_y + v_z \partial_z$$

For this type of flows only x - components sustains which is $v_x \partial_x$,

Therefore

$$v_x \partial_x \tau_p = 0$$

Following expressions are the part of constitutive equation

$$-\{\nabla \mathbf{V}^T \cdot \boldsymbol{\tau}_p\} = \begin{bmatrix} \tau_{xy} & \tau_{yy} & \tau_{yz} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \dot{\gamma} \quad (5.14)$$

The transpose of equation (5.14) can be written as:

$$-\{\boldsymbol{\tau}_p \cdot \nabla \mathbf{v}\} = \begin{bmatrix} \tau_{xy} & 0 & 0 \\ \tau_{yy} & 0 & 0 \\ \tau_{yz} & 0 & 0 \end{bmatrix} \dot{\gamma} \quad (5.15)$$

With the help of equation (5.14) and equation(5.15) the constitutive equation of Hookean dumb-bell model can be expressed as:

$$\begin{bmatrix} \tau_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{xy} & \tau_{yy} & \tau_{yz} \\ \tau_{xz} & \tau_{yz} & \tau_{zz} \end{bmatrix} + \lambda \begin{bmatrix} -2\tau_{xy} & \tau_{yy} & \tau_{yz} \\ -\tau_{yy} & 0 & 0 \\ -\tau_{yz} & 0 & 0 \end{bmatrix} \dot{\gamma} = -nkT\lambda \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \dot{\gamma} \quad (5.16)$$

The following equations can be written comparing the left and right side of equation (5.16)

$$\tau_{yy} = \tau_{yz} = \tau_{zz} = 0 \quad (5.17)$$

$$\tau_{xz} - \lambda\tau_{yz}\dot{\gamma} = 0 \quad (5.18)$$

$$\tau_{xx} - 2\lambda\tau_{xy}\dot{\gamma} = 0 \quad (5.19)$$

and

$$\tau_{xy} = -nkT\lambda\dot{\gamma} \quad (5.20)$$

Again the equations (5.19) and (5.20) are simplified as

$$\tau_{xy} = -nkT\lambda\dot{\gamma} \quad (5.21)$$

$$\tau_{xx} = -2nkT\lambda^2\dot{\gamma}^2 \quad (5.22)$$

Dividing equation(5.21) by $\dot{\gamma}$ and (5.22) by $\dot{\gamma}^2$, we get,

$$\eta(\dot{\gamma}) = -\frac{\tau_{xy}}{\dot{\gamma}} = nkT\lambda \quad (5.23)$$

$$\psi(\dot{\gamma}) = -\frac{\tau_{xx}}{\dot{\gamma}^2} = 2nkT\lambda^2 \quad (5.24)$$

Also the second normal stress difference is zero i.e.

$$\psi_2 = 0 \quad (5.25)$$

From equations (5.23) and (5.24) ,it is clear that all the steady shear flow material functions are shear independent. This why this model is still not realistic. Also the Hookean force allows the spring to be extended to any large length,which is not the property of real polymer molecules. Due to this reason, finitely elongated FENE-P model is introduced.

5.4 The FENE-P dumbbell model

FENE means finitely elongated non linear elastic and P means statistical closure proposed by Peterlin. So it is the combination of FENE dumbbell model and statistical closure proposed by Peterlin for the restoring forces.[Bird et al., 1987b][Peterlin, 1966]

The constitutive equations of FENE dumbbell are derived using kinetic theory. For this model, polymer molecules are considered as elastic dumbbells in dilute solution.

To derive constitutive equations: $\mathbf{F}_c = \frac{HQ}{1 - (\frac{Q}{Q_0})^2}$

The kramer' form,

$$\boldsymbol{\tau}_p = -nH \left\langle \frac{\mathbf{Q}\mathbf{Q}}{1 - \frac{Q^2}{Q_0^2}} \right\rangle + nkT\boldsymbol{\delta} \quad (5.26)$$

Where T represents the temperature and k represents Boltzmann constant.

The Giesekus form,

$$\boldsymbol{\tau}_p = \frac{n\zeta}{4} \langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} \quad (5.27)$$

Now we take Peterlin's closure, and hence the model become FENE-P

Peterlin's Closure :

$$\left\langle \frac{\mathbf{Q}\mathbf{Q}}{1 - \frac{Q^2}{Q_0^2}} \right\rangle \sim \frac{\langle \mathbf{Q}\mathbf{Q} \rangle}{1 - \langle \frac{Q^2}{Q_0^2} \rangle} \quad (5.28)$$

[Bird et al., 1987b][Peterlin, 1966]

So equations (5.26) and (5.27) are can be written as:

$$\boldsymbol{\tau}_p = -nH \frac{\langle \mathbf{Q}\mathbf{Q} \rangle}{1 - \langle \frac{Q^2}{Q_0^2} \rangle} + nkT\boldsymbol{\delta} \quad (5.29)$$

$$\boldsymbol{\tau}_p = \frac{n\zeta}{4} \langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} \quad (5.30)$$

Now taking the trace of equation (5.29), we get:

$$\text{tr}\boldsymbol{\tau}_p = -nH \frac{\langle Q^2 \rangle}{1 - \langle \frac{Q^2}{Q_0^2} \rangle} + 3nkT \quad (5.31)$$

Let $X = Q^2/Q_0^2$, Which is relative mean square elongation.

Then equation (5.31) can be written as:

$$\text{tr}\boldsymbol{\tau}_p = \frac{nHQ_0^2X}{1 - X} + 3nkT \quad (5.32)$$

To get the expression for X ,

$$\frac{nkTbX}{1 - X} = 3nkT - \text{tr}\boldsymbol{\tau}_p \quad (5.33)$$

or,

$$\frac{X}{1 - X} = \frac{3}{b} \left(1 - \frac{\text{tr}\boldsymbol{\tau}_p}{3nkT} \right) = Z - 1$$

Where,

$b = \frac{HQ_0^2}{kT}$ is dimensionless constant called degree of non - linearity parameter and

$Z = \frac{1}{1-X}$ represent the function of trace of stress tensor

$$1 - X = \frac{1}{Z} \text{ and } X = 1 - Z^{-1}$$

Now equation (5.26) becomes,

$$\boldsymbol{\tau}_p = -nHZ \langle \mathbf{Q}\mathbf{Q} \rangle + nkT\boldsymbol{\delta} \quad (5.34)$$

Also from equation (5.27)

$$\boldsymbol{\tau}_p = -\frac{n\zeta}{4} \langle \mathbf{Q}\mathbf{Q} \rangle_{(1)}$$

Or,

$$\langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} = -\frac{4\boldsymbol{\tau}_p}{n\zeta} \quad (5.35)$$

The oldroyd derivative of equation (5.34) gives

$$\boldsymbol{\tau}_{p(1)} = -nH (Z \langle \mathbf{Q}\mathbf{Q} \rangle)_{(1)} - nkT\dot{\boldsymbol{\gamma}} \quad (5.36)$$

To evaluate, $(Z \langle \mathbf{Q}\mathbf{Q} \rangle)_{(1)}$,

$$(Z \langle \mathbf{Q}\mathbf{Q} \rangle)_{(1)} = \frac{D}{Dt}(Z \langle \mathbf{Q}\mathbf{Q} \rangle) - \{\boldsymbol{\nabla}\mathbf{v}^T \cdot Z \langle \mathbf{Q}\mathbf{Q} \rangle\} - \{Z \langle \mathbf{Q}\mathbf{Q} \rangle\} \cdot \boldsymbol{\nabla}\mathbf{v} \quad (5.37)$$

The right side of equation (5.37) is

$$\frac{D}{Dt}(Z \langle \mathbf{Q}\mathbf{Q} \rangle) - Z \{ \{ \nabla \mathbf{v}^T \cdot \langle \mathbf{Q}\mathbf{Q} \rangle \} + \{ \langle \mathbf{Q}\mathbf{Q} \rangle \cdot \nabla \mathbf{v} \} \} = \quad (5.38)$$

The derivative of first term of equation (5.38) gives

$$\frac{DZ}{Dt} \langle \mathbf{Q}\mathbf{Q} \rangle + Z \frac{D \langle \mathbf{Q}\mathbf{Q} \rangle}{Dt} - Z \{ \{ \nabla \mathbf{v}^T \cdot \langle \mathbf{Q}\mathbf{Q} \rangle \} + \{ \langle \mathbf{Q}\mathbf{Q} \rangle \cdot \nabla \mathbf{v} \} \} \quad (5.39)$$

using the values of this equation , equation (5.35) can be written as

$$\frac{DZ}{Dt} \langle \mathbf{Q}\mathbf{Q} \rangle + Z \langle \mathbf{Q}\mathbf{Q} \rangle_{(1)} = \frac{DZ}{Dt} \langle \mathbf{Q}\mathbf{Q} \rangle - 4Z \frac{\tau_p}{n\zeta} \quad (5.40)$$

now from Kramer' equation,

$$\langle \mathbf{Q}\mathbf{Q} \rangle = \frac{1}{nHZ} [-\tau_p + nkT\delta]$$

$$\tau_p_{(1)} = -nH \left[\frac{DZ}{Dt} \langle \mathbf{Q}\mathbf{Q} \rangle - z \cdot \frac{4\tau_p}{n\zeta} \right] - nkT\dot{\gamma} \quad (5.41)$$

If the equation (5.41) multiplied by λ , we get:

$$Z\tau_p + \lambda\tau_p_{(1)} + \lambda nH \frac{DZ}{Dt} \langle \mathbf{Q}\mathbf{Q} \rangle = -nkT\lambda\dot{\gamma} \quad (5.42)$$

From equation (5.34),

$$nH \langle \mathbf{Q}\mathbf{Q} \rangle = -\frac{1}{Z} [\tau_p - nkT\delta] \quad (5.43)$$

With the help of equation (5.43), equation (5.42) becomes

$$Z\boldsymbol{\tau}_p + \lambda\boldsymbol{\tau}_p^{(1)} - \lambda[\boldsymbol{\tau}_p - nkT\boldsymbol{\delta}] \frac{D \ln Z}{Dt} = -nkT\lambda\dot{\gamma} \quad (5.44)$$

This is the constitutive equation(5.44) of FENE-P dumbbell model with

$$Z = 1 + \frac{3}{b} \left(1 - \frac{\text{tr}\boldsymbol{\tau}}{3nkT} \right)$$

6 FENE-P bead-spring-chain model

In FENE-P model , two beads were considered connected with a springs . But in case of this finitely extensible bead-spring-chain model, polymeric chain with N beads are connected through N - 1 springs and these Beads and springs are identical. Also the spring which connects the beads has spring constant H with maximum length Q_o . On the basis of N , the degradation of polymer molecule will be considered further in diluted solution . Here a simplified model (not necessarily realistic) of mechanical degradation will be considered which is gradual erosion from the ends of the chains. Effectively , this means a decrease in N, the number concentration of molecules n being unchanged. Similarly different degradation schemes can be considered using this polymer model as a framework.

The stress tensor due to the contribution of solvent and polymer is:

$$\boldsymbol{\tau} = -\eta_s \dot{\boldsymbol{\gamma}} + \sum_{j=1}^{N-1} \boldsymbol{\tau}_j \quad (6.1)$$

[Bird et al., 1980]

The constitutive equation for this model is given by:

$$Z_j \boldsymbol{\tau}_j + \lambda_j \boldsymbol{\tau}_{j,(1)} - \lambda_j \{ \boldsymbol{\tau}_j - nkT \boldsymbol{\delta} \} \frac{D \ln Z}{Dt} = -nkT \lambda_j \dot{\boldsymbol{\gamma}} \quad (6.2)$$

[Bird et al., 1980]

where

$$Z_j = 1 + \frac{3}{b} \left(1 - \frac{\text{tr} \boldsymbol{\tau}_j}{3nkT} \right) \quad (6.3)$$

and

$$\lambda_j = \frac{\lambda}{2 \sin^2 \left(\frac{j\pi}{2N} \right)} \quad (6.4)$$

Further, the material functions of dumbbell model and FENE - bead - spring chain model will be considered and degradation of polymer molecules will be examined as possible.

6.1 Material functions

The material functions are as follow:

6.1.1 For steady shear flow

For dumbbell

We have,

$$\tau_{xy} = -\eta(\dot{\gamma})\dot{\gamma} \quad (6.5)$$

and

$$\tau_{xx,j} - \tau_{yy,j} = -\psi_1\dot{\gamma}^2 \quad (6.6)$$

For bead - spring - chain - model

$$\tau_{xy,j} = -\eta_j(\dot{\gamma})\dot{\gamma} \quad (6.7)$$

and

$$\tau_{xx,j} - \tau_{yy,j} = -\psi_{1,j}\dot{\gamma}^2 \quad (6.8)$$

For steady shear flow, the constitutive equation (6.2) can be written as,

$$Z_j\tau_{xx,j} - 2\lambda_j\tau_{xy,j}\dot{\gamma} = 0 \quad (6.9)$$

$$Z_j\tau_{xy,j} = nkT\lambda_j\dot{\gamma} \quad (6.10)$$

dividing equation (6.9) by (6.10), we get,

$$\tau_{xx,j} = -\frac{2}{nkT}(\tau_{xy,j})^2 \quad (6.11)$$

or,

$$\psi_{1,j} = \frac{2}{nkT}\eta_j^2 \quad (6.12)$$

Also

$$Z_j = \frac{b+3}{b} - \frac{\text{tr}\tau_j}{bnkT} \quad (6.13)$$

or,

$$Z_j = \frac{b+3}{b} + \frac{2(\tau_{xy,j})^2}{b(nkT)^2} \quad (6.14)$$

with the help of equation (6.14), equation (6.10) can be written as

$$\left(\frac{b+3}{b} + \frac{2(\tau_{xy,j})^2}{b(nkT)^2}\right) \tau_{xy,j} = -nkT\lambda_j\dot{\gamma} \quad (6.15)$$

As we know that,

$-\eta_j\dot{\gamma} = \tau_{xy,j}$ equation (6.14) can be written as:

$$\left(\frac{b+3}{b} + \frac{2(\eta_j\dot{\gamma})^2}{b(nkT)^2}\right) \eta_j\dot{\gamma} = -nkT\lambda_j\dot{\gamma} \quad (6.16)$$

Dividing equation (6.16) by $nkT\lambda_j\dot{\gamma}$, we get,

$$\frac{b+3}{b} \frac{\eta_j}{nkT\lambda_j} + \frac{2(\eta_j\dot{\gamma})^2}{b(nkT)^2} \frac{\eta_j}{nkT\lambda_j} = 1 \quad (6.17)$$

We have,

$$\bar{\eta} = \frac{b+3}{b} \frac{\eta_j}{nkT\lambda_j} \eta_j \quad (6.18)$$

or,

$$\eta_j = \frac{bnkT\lambda_j}{b+3} \bar{\eta} \quad (6.19)$$

With the help of equation (6.19), equation (6.17) can be written as:

$$\bar{\eta} + (\bar{\eta})^3 \frac{2b^2(\lambda_j\dot{\gamma})^2}{(b+3)^3} = 1 \quad (6.20)$$

If $\Lambda = \lambda \dot{\gamma} \cdot \sqrt{\frac{2b^2}{(b+3)^2}}$ and $\lambda_j = 2c_j \lambda$, equation (6.20) can be written as

$$(\bar{\eta})^3 (2c_j \Lambda)^2 + \bar{\eta} - 1 = 0 \quad (6.21)$$

Equation (6.21) is the master equation of η and η_j . Also $\bar{\eta}(\Lambda)$ is known function which is the solution of equation (6.21)

for the dumbbell,

$$\lambda_j = \lambda \text{ and } 2c_j = 1$$

$$\eta = \frac{b}{b+3} nkT \lambda \bar{\eta}(\Lambda) \quad (6.22)$$

where

$$\frac{b}{b+3} nkT \lambda = \eta_o$$

$$\psi_1 = \frac{2b^2}{(b+3)^2} nkT \lambda^2 \bar{\eta}^2(\Lambda) \quad (6.23)$$

where

$$\frac{2b^2}{(b+3)^2} nkT \lambda^2 = \psi_{1,0}$$

If shear rate is low, Λ is very small the master equation (6.21) implies that $\bar{\eta} \rightarrow 1$. This is why for dumbbell, equation (6.22) becomes

$$\bar{\eta} = \frac{\eta}{\eta_o} \quad (6.24)$$

For the bead - spring - chains

$$\eta_j = \frac{b}{b+3} nkT \lambda 2c_j \bar{\eta}(2c_j \Lambda) \quad (6.25)$$

Or,

$$\eta_j = \eta_{0,DB} 2c_j \bar{\eta}(2c_j \Lambda) \quad (6.26)$$

And similarly

$$\psi_{1,j} = \psi_{1,0,DB}(2c_j)^2 \cdot \bar{\eta}^2(2c_j\Lambda) \quad (6.27)$$

Finally, viscosity and first normal stress difference for bead - spring - chain model can be written as:

$$\eta = \eta_{0,DB} \cdot \sum_{j=1}^{N-1} 2c_j \bar{\eta}(2c_j\Lambda) \quad (6.28)$$

$$\psi_1 = \psi_{1,0,DB} \cdot \sum_{j=1}^{N-1} (2c_j)^2 \bar{\eta}^2(2c_j\Lambda) \quad (6.29)$$

The graph between scaled viscosity and scaled shear rate for bead - spring - chain model is as shown in figure 16 below.

This graph is plotted between scaled viscosity and scaled shear rate. The degree of degradation is increased with the decrease of number N . It is seen that at any fixed $\dot{\gamma}$, the viscosity decreases as N decreases. Power law index is unchanged for all values of N (asymptotic part). onset of thinning is shifted to the right i.e. towards the higher values of $\dot{\gamma}$

To describe the degradation of polymer molecule , let us assume first low shear rate i.e. zero - shear - rate in which condition: $\bar{\eta} \rightarrow 1$

So the zero -shear-rate viscosity of this model can be written as

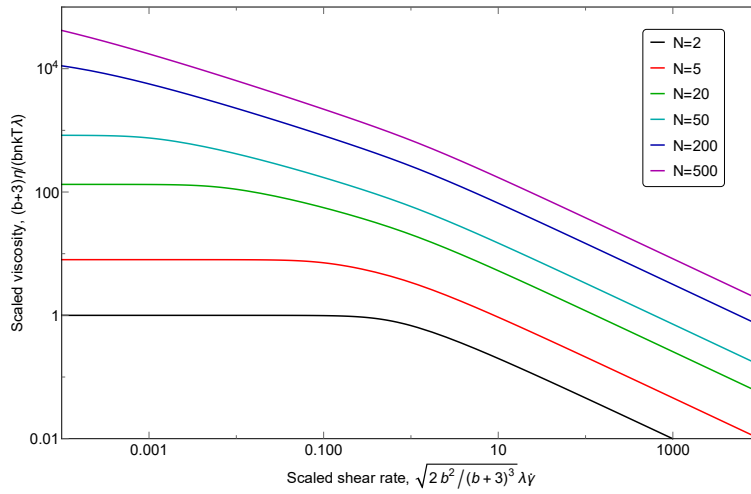


Figure 16: Variation of viscosity with shear rate

$$\eta_0 = \eta_{0,DB} \sum_{j=1}^{N-1} (2c_j) = \eta_{0,DB} \frac{N^2 - 1}{3} \quad (6.30)$$

where

$$\sum_{j=1}^{N-1} (c_j) = \frac{N^2 - 1}{6}. \quad (6.31)$$

[Chen, 2002]

let N_1 be the number of beads before degradation and N_2 be the number of beads after degradation such that $N_1 > N_2$.

Then

$$\frac{\eta_{0, before}}{\eta_{0, after}} \sim \frac{N_{before}^2}{N_{after}^2} \sim \frac{1}{(\text{degree of degradation})^2}$$

Also the degradation percentage can be written as:

$$\text{percentage degradation} = \left(1 - \frac{N_{after}}{N_{before}}\right) 100$$

This kinds of predictions can be tested experimentally.

The first normal stress difference for this model at zero - shear- rate can be written as:

$$\psi_{1,0} = \psi_{1,0,DB} \sum_{j=1}^{N-1} (2c_j)^2 = \psi_{1,0,DB} \frac{(N^2 - 1)(2N^2 + 7)}{45} \quad (6.32)$$

where

$$\sum_{j=1}^{N-1} (2c_j)^2 = \frac{(N^2 - 1)(2N^2 + 7)}{180} \quad (6.33)$$

[Chen, 2002]

For high shear limit, the master equation is

$$\bar{\eta}^3 \Lambda^2 + \bar{\eta} = 1 \quad (6.34)$$

At high shear rate Λ^2 becomes very high and we can neglect $\bar{\eta}$ for dumbbell,

$$\bar{\eta} \sim \Lambda^{-\frac{2}{3}} \quad (6.35)$$

Hence for the bead - spring - chain model, the viscosity at high shear rate is given by

$$\eta \sim \eta_{0,DB} \sum_{j=1}^{N-1} 2c_j (2c_j \Lambda)^{-\frac{2}{3}} \quad (6.36)$$

Or,

$$\eta \sim \eta_{0,DB} \sum_{j=1}^{N-1} 2^{\frac{1}{3}} c_j^{\frac{1}{3}} \Lambda^{-\frac{2}{3}} \quad (6.37)$$

Similarly , the first normal stress difference for bead - spring - chain - model at high shear rate is given by

$$\psi_1 \sim \psi_{0,DB} \sum_{j=1}^{N-1} (2c_j)^2 \Lambda^{\frac{-4}{3}} (2c_j)^{\frac{-4}{3}} \quad (6.38)$$

Or,

$$\psi_1 \sim \psi_{0,DB} \sum_{j=1}^{N-1} 2^{\frac{2}{3}} \Lambda^{\frac{-4}{3}} c_j^{\frac{2}{3}} \quad (6.39)$$

Trigonometric sums such as $\sum_{j=1}^{N-1} c_j^{\frac{1}{3}}$ and $\sum_{j=1}^{N-1} c_j^{\frac{2}{3}}$ need to be investigated in more details. This is to be discussed elsewhere.

For dumbbells

$$\psi_1 = \frac{2}{nkT} \eta_0^2 \quad (6.40)$$

$$\psi_{1,0} = \frac{2}{nkT} \eta_0^2 \quad (6.41)$$

A useful relation.

$$\eta_0 \lambda_e = \eta_0 \frac{3\lambda}{b+3} \frac{nkT}{nkT} = \frac{\eta_0^2}{nkT} = \frac{1}{2} \psi_{1,0} \quad (6.42)$$

Now,

$$\bar{\psi}'_1 = \frac{\psi'_1}{\psi_{1,0,DB}} = \frac{1 - 2\Lambda_e^2}{2(1 + \Lambda_e^2)(1 + 4\Lambda_e^2)} \quad (6.43)$$

Finally,

$$\frac{\psi'_{1,BSC}}{\psi_{1,0,DB}} = \sum_{j=1}^{N-1} 4c_j^2 \bar{\psi}'_1 (2c_j \Lambda_e) \quad (6.44)$$

The cross - plot between ψ_1 and η^2 is as shown in figure 17 below:

The graph shows variation of scaled elastic ratio with scaled shear rate. The black line i.e. N=2 represents the dumbbell limit. It is seen that at low shear rates the ratio reaches a plateau value.

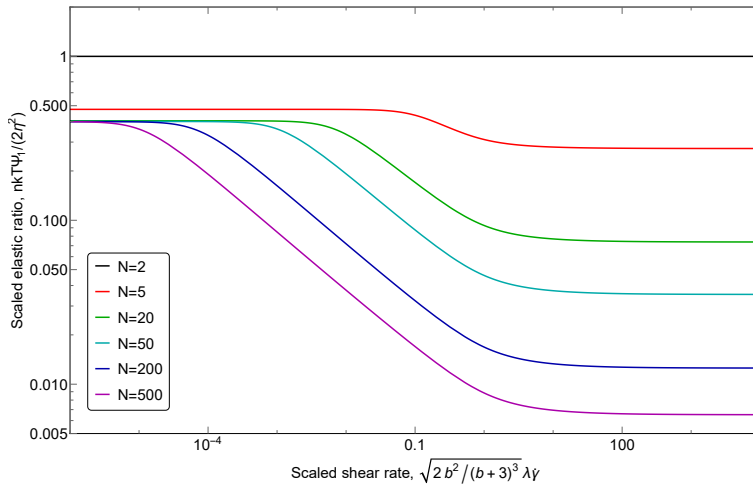


Figure 17: cross plot between ψ_1 and η^2

At low N , this value decreases with N increasing; while at high N , it becomes independent of N . The width of this plateau decreases as N increases. At high shear rates, the ratio reaches another (smaller) plateau value, which also decreases as N increases. The transition region between the two plateaus becomes less pronounced as N decreases and vanishes in the dumbbell limit. These predictions are to be checked experimentally.

6.1.2 Small - amplitude oscillatory shearing (SAOS)

For dumbbell model,

$$\tau_{xy} = -\eta' \dot{\gamma}_0 \cos \omega t - \eta'' \dot{\gamma}_0 \sin \omega t \quad (6.45)$$

But for bead - spring - chain model,

$$\tau_{xy,j} = -\eta'_j \dot{\gamma}_0 \cos \omega t - \eta''_j \dot{\gamma}_0 \sin \omega t \quad (6.46)$$

Also

$$\tau_{xy} = \sum \tau_{xy,j} \implies \eta' = \sum \eta'_{ij} \text{ and } \eta'' = \sum \eta''_{ij}$$

From the constitutive equation, we can write,

$$\frac{b+3}{3} D_{1,j} + \lambda_j \partial_t D_{1,j} - 2\lambda_j \dot{\gamma} \tau_{xy,j} \quad (6.47)$$

we have

$$\lambda_j = 2c_j \cdot \lambda, \lambda_e = \frac{3\lambda}{b+3} \text{ and } \lambda_e = 2c_j \lambda_e$$

Where λ_e is the experimental time constant.

So equation (6.47) can be written as

$$D_{1,j} + 2C_j \lambda_e D_{1,j} - 22c_j \lambda_e \dot{\gamma} \tau_{xy,j} = 0 \quad (6.48)$$

or,

$$\tau_{xy,j} 2c_j \lambda_e \partial_t \tau_{xy,j} = -2c_j \eta_0 \dot{\gamma} \quad (6.49)$$

The right hand side of equation (6.49) represents for the dumbbell because $\eta_0 \implies 2c_j\eta_0$

Hence for the dumbbell, the complex viscosity is

$$\eta' = \frac{\eta_{0,DB}}{1 + (\lambda_e\omega)^2} \quad (6.50)$$

The complex viscosity in case of bead -spring - chain model is given by

$$\eta'_{1,j} = \frac{2c_j\eta_{0,DB}}{1 + (2C_j\lambda_e\omega)^2} \quad (6.51)$$

If $\Lambda_e = \lambda_e\omega$ Then

$$\eta'_{1,j} = 2c_j \cdot \eta'(2c_j\Lambda) \quad (6.52)$$

Therefore the total value is

$$\eta' = \sum_{j=1}^{N-1} 2c_j \eta'_{DB}(2c_j\Lambda_e) \quad (6.53)$$

Similarly for the dumbbell,

$$\eta''_{DB} = \frac{\eta_0\Lambda_e}{1 + (\Lambda_e)^2} \quad (6.54)$$

For the bead - spring - chain model,

$$\eta'' = \sum_{j=1}^{N-1} 2c_j \eta''_{DB}(2c_j\Lambda_e) \quad (6.55)$$

For the dumbbell,

$$\psi'_{1,DB} = \frac{\eta_0\Lambda_e(1 - 2\Lambda_e^2)}{(1 + \Lambda_e^2)(1 + 4\Lambda_e^2)} \quad (6.56)$$

For the bead - spring - chain model,

$$\psi'_1 = \sum_{j=1}^{N-1} 4c_j^2 \psi'_{1,DB}(2c_j\Lambda_e) \quad (6.57)$$

Finally for the dumbbell,

$$\psi''_{1,DB} = \frac{3\eta_0\lambda_e\Lambda_e}{(1 + \Lambda_e^2)(1 + 4\Lambda_e^2)} \quad (6.58)$$

For the bead - spring - chain model,

$$\psi''_1 = \sum_{j=1}^{N-1} 4c_j^2\psi''_{1,DB}(2c_j\Lambda_e) \quad (6.59)$$

Where η' and η'' are the complex viscosity coefficients which are functions of w , ψ' and ψ'' are the complex first normal stress differences respectively.

During oscillatory flow of fluid, the process of deformation and restoration takes place. The parameter $G' = \eta''\omega$ is called the storage modulus. It gives the information about elastic property of fluid or simply predicts the energy stored during the deformation.

Similarly the parameter $G'' = \eta'\omega$ is called loss modulus. It tells about the viscous behaviour of fluid or it can predict the energy dissipated during flow.

For the dumbbell,

$$\frac{\lambda_e \omega \eta'}{\eta_0} = \frac{\omega \lambda_e}{1 + \Lambda_e^2} = \frac{\Lambda_e}{1 + \Lambda_e^2} \quad (6.60)$$

Therefore,

$$\frac{\lambda_e G''}{\eta_0} = \frac{G''}{nkT} = \frac{\Lambda_e}{1 + \Lambda_e^2} \quad (6.61)$$

Similarly,

$$\frac{G'}{nkT} = \frac{\Lambda_e^2}{1 + \Lambda_e^2} \quad (6.62)$$

For the bead - spring - chain model,

$$\frac{G'}{nkT} = \sum_{j=1}^{N-1} G'_{DB}(2c_j \Lambda_e) \quad (6.63)$$

and

$$\frac{G''}{nkT} = \sum_{j=1}^{N-1} G''_{DB}(2c_j \Lambda_e) \quad (6.64)$$

The variation of storage modulus and loss modulus with frequency are as shown in figure 18 and 19 respectively.

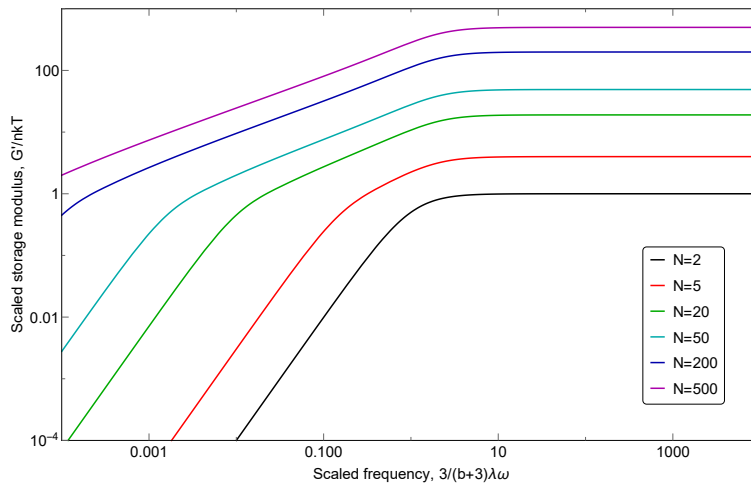


Figure 18: variation of storage modulus with frequency

from the graph , it is cleared that at high frequency, value of storage modulus becomes constant and this constant value increases with increase of N . When polymer molecule degrades , value of G' decreases this means the potential energy stored due to deformation dissipated. Power law region is also observable but narrower and the transition region becomes wider with the increase of value of N

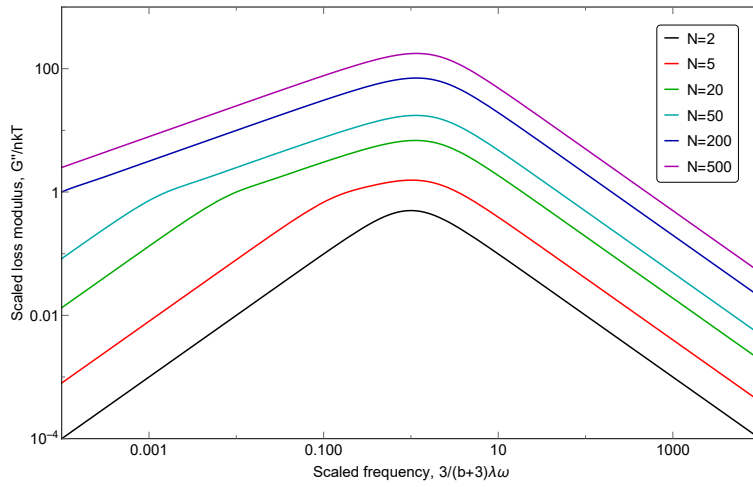


Figure 19: variation of loss modulus with frequency

The graph shows the variation of loss modulus with the frequency. The point of maximum with frequency is independent of N . Power law index remain constant at high frequency. If we go through the experiment, the transition region shall gradually disappear, as the degree of degradation increases.

7 Conclusion

The FENE-P bead - spring - chain model looks suitable model to describe the degradation of polymer molecules. It is considered simple degradation schemes here but this model can describe all types of degradation. The material functions for this model are derived and scaled plots are made for them through which the degradation scheme is studied. It is possible to predict how degradation is going to affect the material functions and these prediction can be verified experimentally.

Remarks:

In more realistic modeling, Hydrodynamic interaction also need to be taken into account. The empirical expression given by Thurston's for hydrodynamic interaction is: [Thurston, 1974] and [Bird et al., 1980]

$$\bar{c}_j = c_j k^{-1} (N/j)^\sigma \quad (7.1)$$

where,

$$k = 1 - 1.66h^*0.78 \quad (7.2)$$

$$\sigma = -1.40h^*0.78 \quad (7.3)$$

and h^* is the hydrodynamic interaction parameter which is dimensionless and given by

$$h^* = (\zeta/\eta_s)(H/36\pi^3kT)^{1/2} \quad (7.4)$$

If this effect is considered ,then the result may be affected.

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