EFFECT OF CONCENTRATION OF WATER-SOLUBLE POLYMER SOLUTIONS ON RHEOLOGICAL PROPERTIES

A Thesis
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by

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Certification

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Abstract

This research deals with experimental study of the rheological behavior of polymer solutions. All polymers studied in this work are water soluble and used in industries as rheology control additives (rheology modifiers), these are: XC-polymer, Carboxymethyl cellulose (two types), Hydroxyethyl cellulose and Polyvinyl alcohol.

The rheological properties of these polymer solutions was investigated using a Couette coaxial cylinder rotational viscometer (Fann model 35A), by measuring shear stresses versus shear rates (i.e. the flow curve).

55 experiments were performed with different polymer concentrations and at 30 °C (±1 °C).

By using the Solver Add-in in Microsoft Excel®, the power law flow model was found to be the best fits the experimental results.

It was found that as polymer concentration increased, the flow behavior index (*n*) decreased and the consistency index (*k*) increased. This behavior reflects the fact that as polymer concentration increases, the solution become far from Newtonian.

Correlations that describe the effect of polymer concentration on *n* and *k* (for each polymer used in this study) was found and presented in a linear and exponential form respectively.

Also it was found that XC-polymer solutions have a higher viscosity, and its viscosity decreases much more than other polymer solutions used in this study.

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Nomenclature

Symbol	**Meaning**	**Unit**
a	Area	m^2
A, B, C	Parameters in Equation (2.12)	-
A', B', C'	Parameters in Equation (2.13)	-
E	Young's modulus	N/m^2
F	Force	N
h	Length of inner cylinder	m
H	Height	m
k	Consistency index	-
k_1, k_2, k_2	Conversion factors in Equations (4.1) and (4.2)	-
l	Length	m
l_o	Initial length	m
M	Torque	N.m
n	Flow behavior index	-
N	Rotational speed	rpm
r	Radius	m
R_c	Radius of the cone	m
R_i	Radius of inner cylinder	m
R_o	Radius of the outer cylinder	m
t	Time	s
V	Velocity	m/s
P	Pressure	Pa

Symbol	**Meaning**	**Unit**

Greek Letters

α	Constant	-
$\dot{\gamma}$	Shear rate	s^{-1}
Δp	Pressure difference	N/m^2
ε	Strain or deformation	-
θ	Dial reading	deg
η	Viscosity	Pa. s
η_∞	Newtonian limiting viscosity	Pa.s
ρ_l	Density of the liquid	kg/m^3
ρ_s	Density of the sphere	kg/m^3
σ	Normal stress	Pa
τ	Shear stress	Pa
τ_m	Shear stress at mean viscosity	Pa
τ_o	Yield stress	Pa
Ω	Angular velocity	rad./s

Abbreviations

CMC	Carboxymethyl Cellulose
PVA	Polyvinyl Alcohol
HEC	Hydroxyethyl Cellulose
XC	Xanthamonas Campestris

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Chapter One

Introduction

Rheology is the study of the deformation and flow of matter. Eugene Bingham, coined the term rheology in 1920, inspired by Heraclitus of Ephesus (536-470 BCE) famous expression παντα ρει: panta rhei, "everything flows". This expression is taken from the more complete quote: “Everything flows and nothing abides: everything gives way and nothing stays fixed” [1].

Rheology is the study of the flow of materials that behave in an interesting or unusual manner. In transport phenomena one limits oneself in general to the study of simple Newtonian liquids or gases, whereas in the rheology the flow behavior of more complicated systems is studied [2].

Deformation is the relative displacement of points of a body. It can be divided into two types: flow and elasticity. Flow is irreversible deformation; when the stress is removed the material does not revert to its original form. This means that the work converted to heat. Elasticity is reversible deformation; the deformed body recovers its original shape, and the applied work is largely recoverable. Vescoelastic materials show both flow and elasticity, which bounces like a rubber ball when dropped, but slowly flows when allowed to stand [3].

Many flow models have been proposed, which are useful for the treatment of experimental data or for describing flow behavior [3]. Such mathematical models range from the very simple to the very complex. Some of them merely involve the plotting of data on graph paper; others require calculating the ratio of two numbers. Some are quite sophisticated and require use computers. This kind of analysis is the best way for getting the most from our data and often results in one of two constants which summarize the data and can be related to product or process performance.

Once a correlation has been developed between rheological data and product behavior, the procedure can then be reversed and rheological data may be used to predict performance and behavior [4].

Viscosity is a principal parameter when any flow measurements of fluids, such as liquids, semi-solids, gases and even solids are made. There are many different techniques for measuring viscosity, each suitable to specific circumstances and materials. The selection of the right viscometer from the scores of instruments available to meet the need of any application is a difficult proposition. Today's instruments vary from the simple to the complex: from counting the seconds for a liquid to drain off a stick to very sophisticated automatic recording and controlling equipment [4].

In polymer solutions, polymer molecules are long chain molecules composed of many repeating units. The bonds along the polymer backbone are continually rotating, and as a result, the molecule itself is continually changing orientation and configuration on a length scale much smaller than the equilibrium size.

In dilute polymer solutions, the rheology of solution is dependent solely on the dynamics of an individual chain and the number of chains (i.e. concentration) in the system. At high concentrations, interactions between polymer molecules impact the rheology in a significant way. As concentration further increases, polymer solutions exhibit a change from fluid-like to more elastic-like behavior [5].

Aim of this work:

1. To study experimentally the rheological behavior of water-soluble polymer solutions.
2. To study the variation of rheological properties with the concentration of each polymer.
3. To compare between the rheological properties of different polymers.

Chapter Two

Literature Survey

2.1 Definition of the Basic Rheological Notions

2.1.1 Deformation

Deformation is a change in shape due to an applied force. This can be a result of tensile (pulling forces) or of compressive (pushing forces) loads being applied [2].

2.1.1.1 Elastic deformation

Elastic deformation as shown in Figure (2.1) applies only to elastic solids.

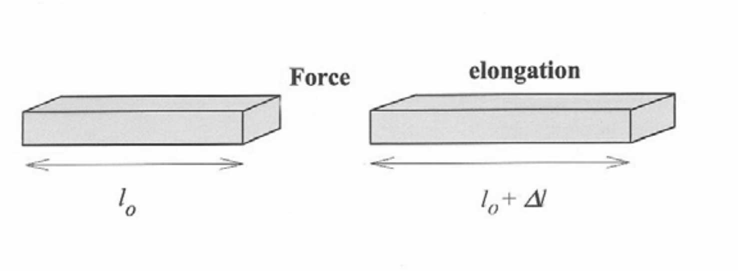


Figure (2.1): Elastic deformation.

Strain or deformation is defined as:

$$\varepsilon = \frac{\Delta l}{l_o} \qquad \ldots(2.1)$$

Stress is the internal distribution of forces within a body that balance and react the loads applied to it. In other words: stress = Force / unit area.

In between stress and strain exits a linear relation given by Hooke's law which is valid only in perfectly elastic bodies [2]:

$$\sigma = E\ \varepsilon \qquad \ldots(2.2)$$

where E is Young's modulus [N/m^2]

2.1.1.2 Shear deformation

Shear stress is a stress state where the shape of a material tends to change (usually by sliding forces) without particular volume change [2].

When a shear deformation with a constant speed applied on a liquid, the flow phenomenon takes place [3]. Figure (2.2) illustrates the concept. A fluid is bounded by two large parallel plates. The area A, separated by a small distance *H*, the bottom plate is held fixed. Application of a force F to the upper plate causes it to move at a velocity *V*. The fluid continuous to deform as long as the force is applied, unlike a solid, which would undergo only a finite deformation [6].

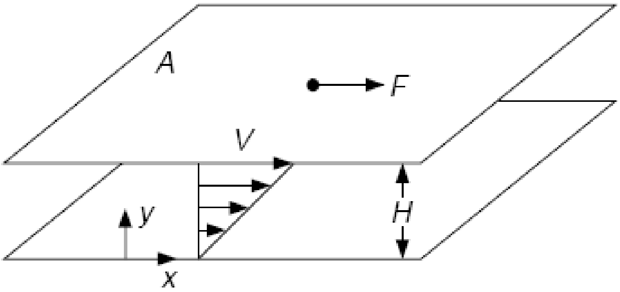


Figure (2.2) Shear deformation in space [6].

The force is directly proportional to the area of the plate. Within the fluid a linear velocity profile is established, due to non-slip condition, the fluid bounding the lower plate has zero velocity and the fluid bounding the upper plate move at plate velocity *V*. The flow in Figure (2.3) is a simple shear flow.

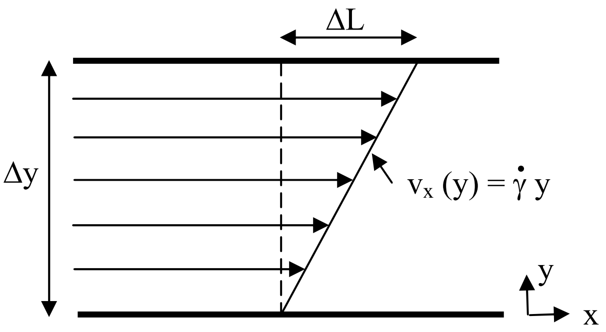


Figure (2.3) Shear deformation of a fluid placed in between two parallel planes [2].

The next formulas are derived in accordance with Figure (2.3).

$$\tau = \frac{F}{A} = -\eta \frac{\Delta v}{\Delta y} \qquad \ldots(2.3)$$

where A = surface area of the plate (m^2)
η = viscosity (Pa. s)
Δv = relative velocity of upper plate ($m. s^{-1}$)
Δy = distance between two plates (m)
$\Delta v / \Delta y$ = shear rate, rate of strain

2.1.2 Shear rate

The shear rate, $\dot{\gamma}$, is the time dependent response of a fluid to any force acting on it. It is the time derivative of the strain $\gamma = \Delta L / \Delta y$, where ΔL is the deformation of the body as a result of the applied stress [2].

Shear rates of typical familiar material and processes are presented in Table (2.1). Sedimentation of particle may involve very low shear rates, spray drying will involve high shear rates, and pipe flow of fluid will usually occur over a moderate shear rate range [7].

Table (2.1) Shear rates of typical familiar material and processes [7].

Situation	Shear rate (1/s)	Application
Sedimentation of particles in a suspending liquid	$10^{-6} - 10^{-3}$	Medicines, paints, spice in salad dressing
Leveling due to surface tension	$10^{-2} - 10^{-1}$	Frosting, paints, printing inks
Draining under gravity	$10^{-1} - 10^{1}$	Vats, small food containers, painting and coating
Extrusion	$10^{0} - 10^{3}$	Snack and pet foods, toothpaste, cereals, polymers
Pouring from a bottle	$10^{1} - 10^{2}$	Food, cosmetics, toiletries
Chewing and swallowing	$10^{1} - 10^{2}$	Foods
Dip coating	$10^{1} - 10^{2}$	Paints, Confectionary
Mixing and stirring	$10^{1} - 10^{2}$	Food processing
Pipe flow	$10^{0} - 10^{3}$	Food processing, blood flow
Rubbing	$10^{2} - 10^{4}$	Topical application of creams and lotions
Brushing	$10^{3} - 10^{4}$	Brushing, painting, lipstick, nail polish
Spraying	$10^{3} - 10^{5}$	Spray drying, spray painting, fuel atomization
High speed coating	$10^{4} - 10^{6}$	Paper
Lubrication	$10^{3} - 10^{7}$	Bearings, gasoline engines

2.1.3 Viscosity

The definition of viscosity implies the existence of laminar flow, which is a movement of one layer of fluid past another with no mass transfer from one to another. Only momentum transfer takes place in this case.

Viscosity is the measure of the internal friction between these layers. This friction becomes apparent when a layer of fluid is made to move relatively to another layer. There is a certain maximum speed at which one layer of fluid can move with relation to another, beyond which an actual transfer of mass occurs. This is called turbulence. The greater the friction the greater the amount of force required causing this movement, which is called shear. The shear occurs whenever the fluid is physically moved by pouring, spreading, spraying, mixing etc. High viscous liquids require more force to move than less viscous liquids [2].

A fluid is called Newtonian when τ and $\dot{\gamma}$ are linearly dependent and their proportionality constant, here the viscosity is constant, independent of $\dot{\gamma}$ [8].

$$\tau = \eta \, \dot{\gamma} \qquad \ldots(2.4)$$

The term viscosity has no meaning for a non-Newtonian fluid unless it is related to a particular shear rate $\dot{\gamma}$. An apparent viscosity can be defined as:

Apparent viscosity $\eta \; (\dot{\gamma}) = \tau / \dot{\gamma}$

The fundamental unit of viscosity is the **poise.** A material requiring a shear stress of one dyne per square centimeter to produce a shear rate of s^{-1} has a viscosity of one Poise. One Pascal – second (Pa.s) equal 10 poise.

2.1.4 Newtonian fluids

Fluids that obey the Newton's law of viscosity (equation (2.3)) are called Newtonian fluids. A Newtonian fluid is a fluid in which shear stress is proportional to the velocity gradient, perpendicular to the plane of shear. The constant of proportionality is known as the viscosity, is a property of the liquid material with the unit Ns/m^2 or Pa.s [2].

The constant of proportionality, η (or the ratio of the shear stress to the rate of shear) which is called the Newtonian viscosity is, by definition, independent of shear rate ($\dot{\gamma}$) or shear stress (τ) and depend only on the material and its temperature and pressure. The plot of shear stress against shear rate for a Newtonian fluid, the so called "flow curve", is therefore a straight line of slop η , and passing through the origin. Figure (2.4) explain the situation [8].

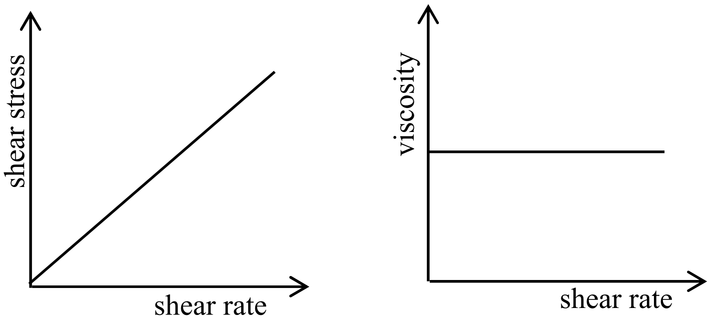


Figure (2.4) Newtonian dependence for shear rate, shear stress and viscosity.

Examples of Newtonian liquids are: water, benzene, hexane and most solutions of simple molecules. At a given temperature the viscosity of a Newtonian fluid remains constant with time for shear state.

2.1.5 Non – Newtonian fluids

A non-Newtonian fluid is a fluid in which shear stress is not simply proportional solely to the velocity gradient, perpendicular to the plane of shear. Non-Newtonian fluids may not have a well-defined viscosity, the viscosity changes as the shear rate is varied. For the viscosity measurements, the viscometer model and other physical parameters might influence the results. The measured viscosity is the **apparent viscosity**, accurate when experimental parameters are taken into account too.

In the category of non-Newtonian fluids one can include most dispersions, blood etc. The viscosity is function of the shear rate. The complexity of the microstructure of the system is influencing the viscosity measurements. If shear forces are applied, the structure of the material may change therefore the viscosity is changing. Rheology can be used to learn about the dispersions' microstructure [2,9].

$$\eta = \eta\,(\dot{\gamma}, \mathrm{Time}) \qquad \ldots(2.5)$$

In equation (2.5), time reflects the structural changes.

There are several types of non-Newtonian flow behavior, characterized by the way a fluid's viscosity changes in response to variations in shear rate.

2.1.5.1 Non – Newtonian fluids – time independent

2.1.5.1.1 Pseudoplastic (shear – thinning) behavior

In this case fluid displays a decreasing viscosity with an increasing shear rate as shown in Figure (2.5). Some examples are paints and emulsions.

The structure of shear-thinning behavior at rest and while flowing is shown in Figure (2.5).

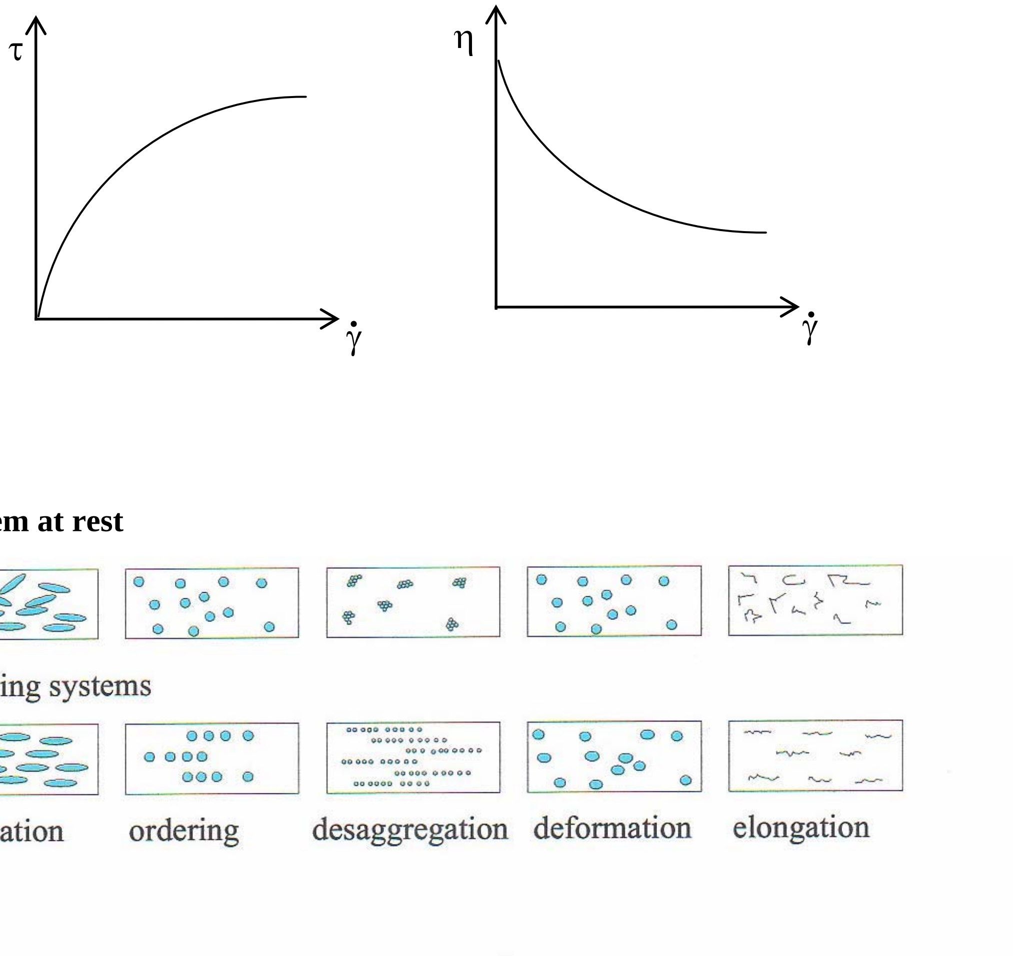


Figure (2.5) Shear thinning behavior and system structure [2].

Power law model describing flow behavior of shear-thinning:

$$\tau = k(\dot{\gamma})^n \qquad n < 1 \qquad \ldots(2.6)$$

2.1.5.1.2 Dilatant (shear – thickening) behavior

An increasing viscosity characterizes dilatant fluids with an increase in shear rate. Examples are some particulate solutions such as: clay slurries, candy compounds, corn starch in water etc.

In these suspensions shear-thickening occurs due to rearrangements in the microstructure evoked by shear.

Power law model describing flow behavior of shear-thickening:

$$\tau = k(\dot{\gamma})^n \qquad n > 1 \qquad \ldots(2.7)$$

Figure (2.6) illustrates the shear – thickening behavior.

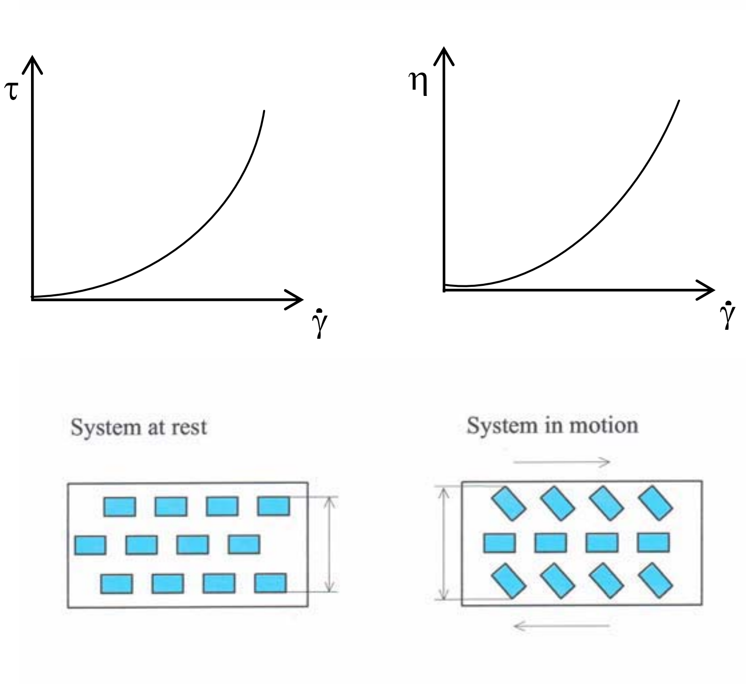


Figure (2.6) Shear thickening behavior and system structure [2].

As conclusion one can see from the equation (2.3), that the viscosity is the proportionality factor between shear stress and shear rate. For Newtonian liquids, η *is* independent of shear rate, but for non – Newtonian fluids the viscosity increases (shear thickening) or decreases (shear thinning) with increasing shear rate [2].

2.1.5.1.5 Bingham behavior

The yield stress in fluids can be defined as the stress (the shear force per unit area) going to a finite nonzero value, the yield stress, while the shear rate (velocity gradient) goes to zero. In practice the yield stress is due to the microstructure of the fluid that resists large rearrangements. Because of the effect of the flow on the system's microstructure, it is in fact impossible to unambiguously define a yield stress [2].

In this case the liquid behaves like a solid under static conditions. A certain amount of force must be applied to the fluid before any flow is induced. This threshold is called the yield stress value. Tomato ketchup is an example of such fluid. Once the yield value is exceeded flow begins. This fluid flow can display Newtonian, Pseudoplastic or dilatant flow characteristics [2].

Figure (2.7) illustrates Bingham behavior.

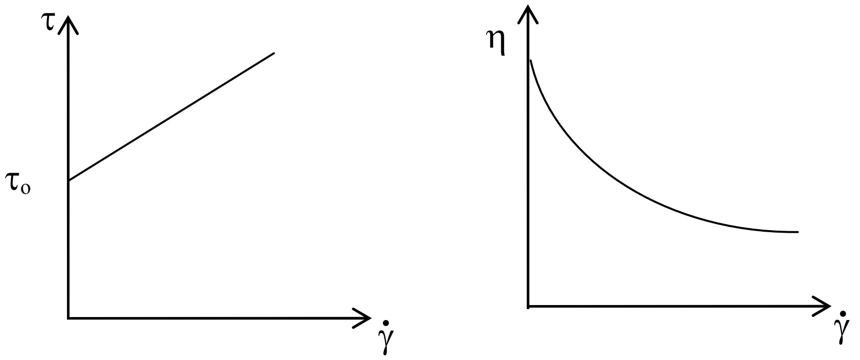


Figure (2.7) Bingham behavior [2].

2.1.5.2 Non – Newtonian fluids – time dependent

Some fluids display a change in viscosity with time, under conditions of constant shear rate. Time-dependent fluid behavior may be further sub-divided into two categories: thixotropy and rheopex or negative thixotropy [9].

2.1.5.2.1 Thixotropic fluids

In this case the fluid undergoes a decrease in viscosity with time, while it is subject to constant shearing as shown in Figure (2.8). As example are greases. It is known from practice that non-dripping paint can flow with decreasing viscosity upon stirring in the paint-pot. Such behavior, where systems that look rather solid like but upon stirring become liquid like, with decreasing viscosity, is called thixotropy. At rest the viscosity increases again, so the paint does not form drips at the wall. Quicksand is also a well-known example of thixotropy: the movements of victim simply decrease the viscosity of the trap and worsen his troubles. The behavior of non- Newtonian fluids is often the result of special structures (networks, colloidal crystals) that are disturbed upon loading. At rest the structures are build up again and consequently the viscosity increases again. If the structure disturbance and build up need some time, then the viscosity is decreasing or increasing with time upon loading or release, respectively [2,9].

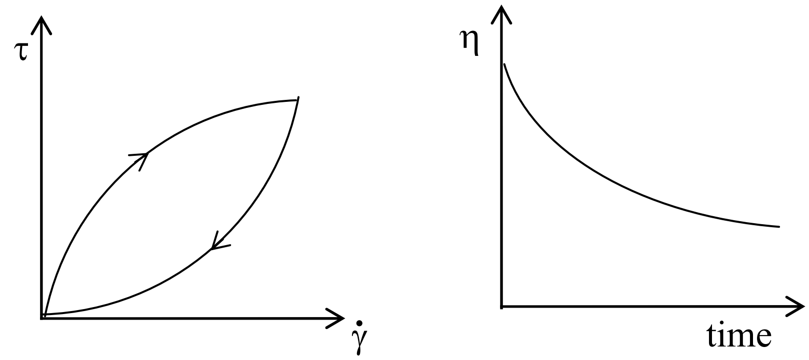


Figure (2.8) Viscosity dependence on time for thixotropic fluids [2].

2.1.5.2.2 Rheopectic fluids

In this case the fluid's viscosity increases with time as it sheared at a constant rate as shown in Figure (2.9).

The apparent viscosity increases with increasing shear rate, the effect is called rheopecty, if time-dependent and dilatancy, if time-independent. Gypsum suspensions are a well-known example of rheopectic fluids.

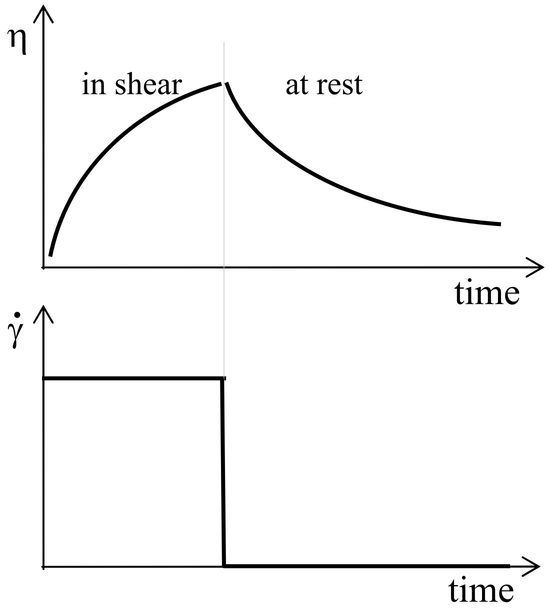


Figure (2.9) Viscosity and shear rate dependence on time for rheopectic fluids [2,10].

2.1.6 Summary of fluid's behaviors

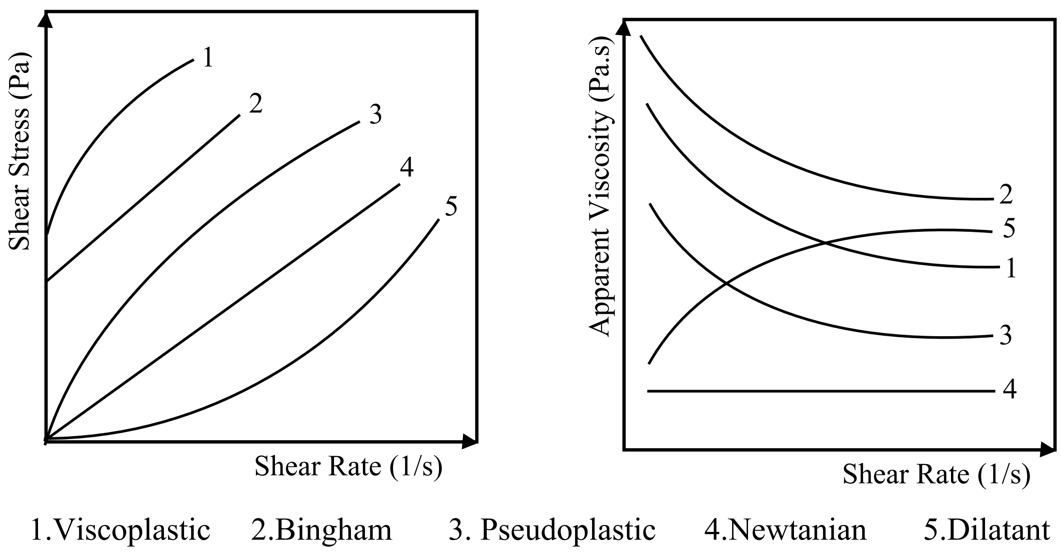


Figure (2.10) Different types of non-Newtonian fluids [2,7].

Materials that completely obey Hook or Newton’s law are rather exceptions than rules: they are called ideally elastic solids (Hookean solids) or ideally viscous liquids (Newtonian liquids). By rheology the flow behavior of more complicated systems, different from Hookean solids or Newtonian liquids that show both elastic and viscous behavior. *Non-linearity* also plays an important role in rheology, the relation between stress and deformation or rate of deformation are non-linear: doubling the force does not necessarily mean that the deformation or rate of deformation also double. In the rheological classification of material the viscosity plays an important role. In the shear stress versus shear rate plot the curves for Newtonian liquids are lines (4) in Figure (2.10). An example of non-linear viscosity is *shear - thinning*, which is a reduction of viscosity with increasing shear rate in steady flow. It means that curves are bending down (3). This arises in suspensions consisting of asymmetrical, stiff particles or of elastic particles that in unloaded form might be symmetrical (polymer melts and solutions). Other systems are characterized by a yield stress, a minimum shear stress, below which no shear flow will take place. These systems are called *plastic* (1) (tooth paste, modeling clay). They are also called *Bingham liquids* (2). Finally there are systems that increase in viscosity with increasing shear rate. These systems are called *shear thickening or dilatant* (5), examples are: concentrated sand/water suspensions, concentrated aqueous starch suspensions or concentrated lattices [2].

2.1.7 Classification of different types of fluids

Section (2.1) is concluded by providing a list of materials displaying a spectrum of non-Newtonian flow characteristics in diverse applications to give an idea of the ubiquitous nature of such flow behavior [9].

Table (2.3) Some common non-Newtonian characteristics [9].

Practical fluid	**Characteristics**	**Consequence of non-Newtonian behavior**
Toothpaste	Bingham plastic	Stay on brush and behaves more liquid like while brushing
Drilling muds	Bingham plastic	Good lubrication properties and ability to convey derbris
Non-drip paints	Thixotropic	Thick in the tin, thin on the brush
Wallpaper past	Pesedoplastic and Visco-elastic	Good spread ability and adhesive properties
Wet cement aggregates	Dilatant	Permits tamping operations in which small impulses product almost complete settlement
Printing inks	Pesedoplastic	Spead easily in high speed machines yet do not run excessively at low speeds

2.2 Water Soluble Polymers

Polymers are large organic molecules compose of seed extracts (guar, starch), modified cellulose (CMC, HEC), biosynthetic gums (Xanthan), and synthetic polymers (PVA) [11].

The simple molecules, from which polymers are formed, are called monomer which is containing primarily of compounds of carbon. To function as monomer, a compound must have at least two reactive sites at which other monomer units can be joined.

Polymers are either linear or branch. In linear polymers, the macromolecule is a long single chain of monomer units. The linear polymers are either "homopolymers" which are containing repeat units of only one chemical composition, or "copolymers" which are containing two or more repeating units, where they have a different chemical composition. For branch polymers, their chains branch off from each other [11].

The selection of best polymer for a certain application depends on the cost of the polymer and on the performance of the polymer.

2.2.1 Cellulose and cellulose derivatives

Cellulose is a widely used organic polymer. It s extracted from wood and other vegetable products. Wood contains 40 to 50% cellulose [12].

Cellulose is insoluble in water due to strong hydrogen bonding. Thus, water particles do not penetrate the solid particles of cellulose. According to that, chemical modifications must be required to these polymers to become soluble in water.

The most important kinds of chemically modified cellulose are:

2.2.1.1. Sodium Carboxymethyl Cellulose (CMC)

CMC is prepared by the reaction of cellulose with chloroacetic acid in the presence of sodium hydroxide. The molecular structure of CMC is shown in Figure (2.11). It is containing strong carboxyl groups which place it in the anionic polyelectrolyte category.

CMC is mainly consumed in detergent, paint, textile, pulp and paper, ceramics and oil drilling industries [13].

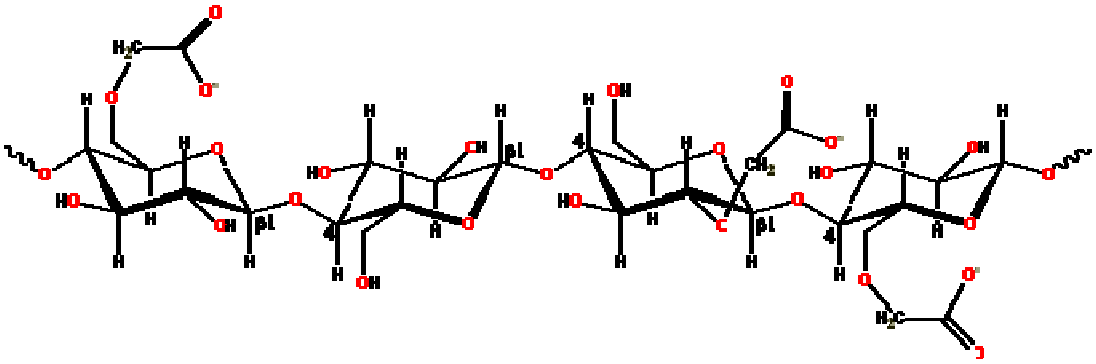


Figure (2.11) Molecular structure of CMC [14].

2.2.1.2. Hydroxyethyl Cellulose (HEC)

HEC is prepared by reaction of alkali cellulose with ethylene oxide in the presence of isopropyl alcohol. The molecular structure of HEC is shown in Figure (2.12).

HEC is used in industry as agent of dispersing, thickening, film-forming etc. In petroleum exploitation, it is used as stabilizer and thickening agent, lubricating agent for well drilling, completing and consolidating to give slurry a good fluidity and stability. Besides, it finds wide application in ink, textile dyeing, paper making, pharmaceuticals, food, agriculture etc [15].

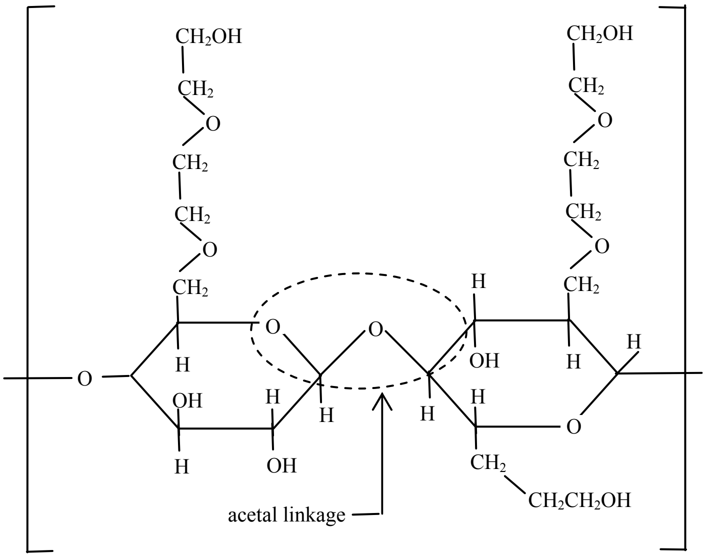


Figure (2.12) Molecular structure of HEC [16].

2.2.2 XC Polymer (Xanthan gum)

XC polymer, also known as Xanthan gum, is an anionic polysaccharide derived from the fermentation of the plant bacteria *Xanthamonas campestris*. It is soluble in hot or cold water and gives visually hazy, neutral pH solution [15]. The molecular structure of XC polymer is shown in Figure (2.13).

Xanthan gum is widely used as an effective stabilizer or a suitable thickener for various kinds of water-based systems. Its numerous area of application cover a broad range including food, pharmaceutical, cosmetic, agricultural, textile, ceramic, and petroleum industries [17,18].

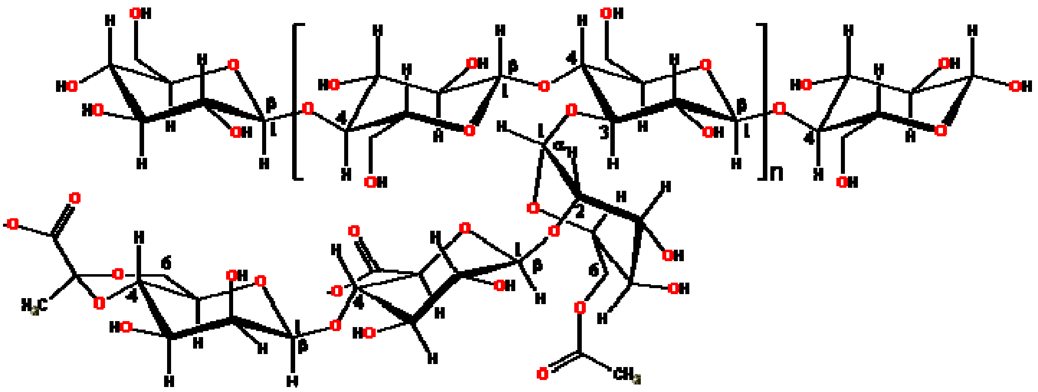
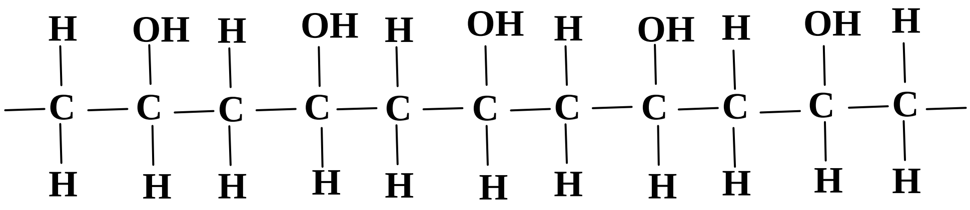


Figure (2.13) Molecular structure of XC polymer [19].

2.2.3 *Polyvinyl Alcohol (PVA)*

Unlike most vinyl polymers, PVA is not prepared by polymerization of the corresponding monomer. PVA instated is prepared by partial or complete hydrolysis of polyvinyl acetate to remove acetate group [20,11]. The molecular structure of PVA is shown in Figure (2.14).



$$\begin{array}{ccccccccccccccccccccccc}
 & H & & OH & & H & & OH & & H & & OH & & H & & OH & & H & & OH & & H & \\
 & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & \\
- & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - \\
 & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & \\
 & H & & H & & H & & H & & H & & H & & H & & H & & H & & H & & H &
\end{array}$$

Figure (2.14) Molecular structure of PVA [20].

Some uses of PVA include [21]:

- Adhesive and thickener material in latex paints, paper coatings, shampoos and glue.
- hoses, gaskets, pipe and gloves where its oil and solvent barrier properties are important.
- As an additive for strength to concrete and cements.

2.3 Polymer Solutions

Polymer molecules are long chain molecules composed of many repeating units. The bonds along the polymer backbone are continually rotating, and as a result, the molecule itself is continually changing orientation and configuration on a length scale much smaller than the equilibrium size.

Polymer solutions can be considered as liquid mixtures made of long macromolecular chains, and small, light molecules of solvent [11].

2.3.1 Polymer dissolution

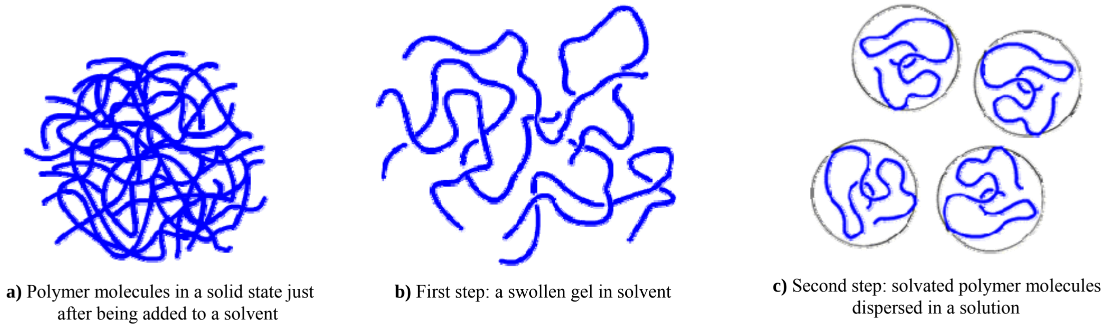
It should be pointed out that not all polymers can be dissolved, and even though when they can, the dissolution process may take up to several days or weeks.

The dissolution of polymers depends not only on their physical properties, but also on their chemical structure, such as: polarity, molecular weight, branching, crosslinking degree, and crystallinity. Polar macromolecules like poly (acrylic acid), poly (acrylamide) and polyvinyl alcohol, among others, are soluble in water. Conversely, nonpolar polymers or polymer showing a low polarity such as polystyrene, poly(methyl methacrylate), poly(vinyl chloride), and poly(isobutylene), are soluble in nonpolar solvents.

Chains containing long branches, cause dense entanglements making difficult the penetration of solvent molecules. Therefore the rate of dissolution in these cases becomes slower than if it was short branching, where the interaction between chains is practically non-existent [22].

There are two stages involved in the dissolution process: in the first place, the polymer swelling, and next the dissolution step itself.

When a polymer is added to a given solvent, attraction as well as dispersion forces begin acting between its segments, according to their polarity, chemical characteristics, and solubility parameter. If the polymer-solvent interactions are higher than the polymer-polymer attraction forces, the chain segment start to absorb solvent molecules, increasing the volume of the polymer matrix, and loosening out from their coiled shape (Figure (2.15b)). The segments are now "solvated" instead of "aggregated", as they were in the solid state [11].


a) Polymer molecules in a solid state just after being added to a solvent

b) First step: a swollen gel in solvent

c) Second step: solvated polymer molecules dispersed in a solution

Figure (2.15). Schematic representation of the dissolution process for polymer molecules [11].

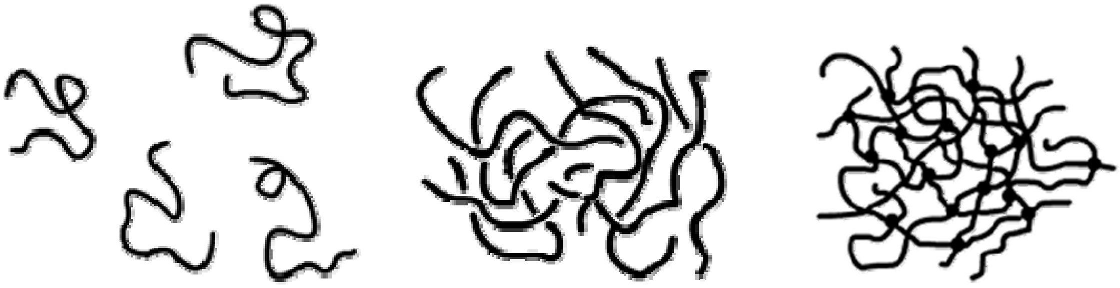
The whole "solvation-unfolding-swelling" process takes a long time, and is influenced only by the polymer-solvent interactions, stirring plays no role in this case. However, it is desirable to start with fine powdered material, in order to expose more of their area for polymer-solvent interactions.

The "solvation-unfolding-swelling" process will continue until *all* segments are solvated. Thus, the whole loosen coil will diffuse out of the swollen polymer, dispersing into a solution. At this stage, the disintegration of the swollen mass can be favored by stirring, which increases the rate of dissolution. The polymer coil, along with solvent molecules held within, adopts a spheric or ellipsoid form, occupying a volume known as *hydrodynamic volume* of the polymer coil (Figure (2.15c)) [11].

2.3.2 Dilute and concentrated polymer solutions

Dilute solutions are those in which each polymer chain is believed (or assumed) to be completely isolated from the other polymer chains, and forms a coil at equilibrium. When the concentration is increased polymer molecules begin to interact by becoming entangled. The concentration (known as the critical concentration) required for a solution to become entangled will decrease as the molecule becomes longer and occupies a larger equilibrium volume.

In response to a deformation, the polymer molecule itself can change both its shape and orientation. In dilute solutions, the rheology of the solution is dependent solely on the dynamics of an individual chain and the number of chains (i.e. the concentration) in the system. At higher concentrations in the entangled region, interactions between polymer molecules due to entanglements impact the rheology in a significant way [11].



a) Dilute solution. b) Concentrated solution. c) Gel.

Figure (2.16). Schematic representation of polymer solutions [11].

There is no interaction at all between the dissolved coils in dilute solutions, as shown in figure (2.16a). Even when the solution is highly viscous, such coils remain as unique entities moving freely among the solvent molecules, without exerting forces of any kind on each other. Consequently, no links can be established between them.

The situation is pretty different in concentrated solutions, represented above in figure (2.16b). As the number of molecules is increased, they are forced to come closer and interaction between them turns noticeable. The summation of intermolecular forces becomes a key factor.

Therefore, the viscosity increases drastically, and the solution begins to exhibit a transition from a concentrated solution to a gel, because such coils will establish linkages at some points, constituting gradually an only giant crosslinked coil, called a *macroscopic gel*. Such macroscopic gel is pictured schematically in figure (2.16c), showing the crosslinks as solid circles [11].

2.4 Flow Models

Many flow models have been proposed, which are useful for the treatment of experimental data or for describing flow behavior. However, it is likely no given model fits the rheological behavior of a material over an extended shear rate range. Nevertheless, these models are useful for summarizing rheological data and are frequently encountered in the literature.

Table (2.4) Flow equations for flow models [3,9].

Flow model	Flow equation	Eqn. no.
Newtonian	$\tau = \eta\dot{\gamma}$	…(2.4)
Bingham plastic	$\tau - \tau_o = \eta\dot{\gamma}$	…(2.8)
Power law	$\tau = k\,\dot{\gamma}^n$	…(2.9)
Modified power law	$\tau - \tau_o = k\,\dot{\gamma}^n$	…(2.10)
Casson fluid	$\tau^{1/2} - \tau_o^{1/2} = \eta_\infty^{1/2}\ \dot{\gamma}^{1/2}$	…(2.11)
Robertson - Stiff	$\tau = A\,(\ \dot{\gamma} + C\ )^B$	…(2.12)
Modified Robertson - Stiff	$\tau - \tau_o = A'\,(\ \dot{\gamma} + C'\ )^B$	…(2.13)
Williamson	$\eta = \eta_\infty + \dfrac{(\eta_o - \eta_\infty)}{1 + \dfrac{\lvert\tau\rvert}{\tau_m}}$	…(2.14)
Cross	$\eta = \eta_\infty + \dfrac{(\eta_o - \eta_\infty)}{1 + \alpha\,\dot{\gamma}^n}$	…(2.15)

Of the models listed in Table (2.4), the Newtonian is the simplest. It fits water, solvents and many polymer solutions over a wide strain rate range. The plastic or Bingham body model predicts constant plastic viscosity above a yield stress. This model works for a number of dispersions including some pigment pastes. Yield stress, τ_o, and plastic (Bingham) viscosity, $\eta_p=(\tau-\tau_o)/\gamma$, may be determined from the intercept and the slope beyond the intercept, respectively, of a shear stress versus shear rate plot [3].

The other models can be applied to non-Newtonian materials where time dependant effects are absent. This situation encompasses many technical important materials from polymer solution to latices, pigment slurries, and polymer melts. At high shear rates most of these materials tend to Newtonian viscosity limit. At low shear rates they tend either to a yield point or to a low shear Newtonian viscosity. At intermediate shear rates, the power low or Casson model is a useful approximation [3].

The power law, $\tau = k\dot{\gamma}^n$, is widely used as a model for non-Newtonian fluids. It holds many solutions and can describe Newtonian, shear-thinning, and shear-thickening behavior, depending on the power factor, *n*, also called the flow behavior index. For a Newtonian fluid, $n=1$ and the equation reduces to Newtonian model. If *n* is less than 1, the fluid is shear thinning; if it is greater than 1, the fluid is shear thickening. A test of whether the power law applies and a means to determining *n* is to plot the log shear stress vs the log shear rate. If the plot is linear the power low applies. The value of n, which is the slope of the line, can be used as a measure of the degree of shear thinning or shear thickening. Dividing the power law equation through by $\dot{\gamma}$ gives an expression in terms of viscosity

$$\eta = k\ \dot{\gamma}^{n-1} \qquad \ldots(2.16)$$

The power model can be extended by including the yield value $\tau - \tau_o = k\dot{\gamma}^n$, which is called the Herschel-Bulkley model, or by adding the Newtonian limiting viscosity, η_∞ . The later is done in the Sisko model, $\eta_\infty + k\dot{\gamma}^{n-1}$. These two models, along with the Newtonian, Bingham, and

Casson models, are often included in data-fitting software supplied for the newer computer-driven viscometers [3].

Another model is the Casson equation, which is useful in establishing the flow characteristics of inks, paint, and other dispersions. An early from this expression (Equation (2.17)) was modified to give Equation (2.18):

$$\tau^{1/2} = k_o + k_1\, \dot{\gamma}^{1/2} \qquad \ldots(2.17)$$

$$\eta^{1/2} = {\eta_\infty}^{1/2} + {\tau_o}^{1/2}\ \dot{\gamma}^{-1/2} \qquad \ldots(2.18)$$

The square root of viscosity is plotted against the reciprocal of the square root of shear rate. The square of the slope is τ_o, the yield stress; the square of the intercept is η_∞, the viscosity at infinite shear rate. No material actually experiences an infinite shear rate, but η_∞ is a good representation of the condition where all rheological structure has been broken down. The Casson stress τ_o is somewhat different from the yield stress discussed earlier in that there may or may not be an intercept on the shear stress-shear rate curve for the material. If there is an intercept, then the Casson yield stress is quite close to that value. If there is no intercept, but the material is shear thinning, a Casson plot gives a value for τ_o that is indicative of the degree of shear thinning [3].

The Williamson equation is useful for modeling shear-thinning fluids over a wide range of shear rates. It makes provision for limiting low and high shear Newtonian viscosity behavior, where τ is the absolute value of shear stress and τ_m is the shear stress at which the viscosity is the mean of the viscosity limits η_o and η_∞ , ie, at $\eta = (\eta_o + \eta_\infty)/2$.

The Cross equation assumes that a shear thinning fluid has high and low limiting viscosity, where α and n are constants. The value for n is often given as 2/3, but polymer melts has shown a wide range of values. The constant α is associated with rupture of the linkages in the structure of the fluid [3].

2.5 Viscometers

Many commercial viscometers are available with a variety of geometries for wide viscosity ranges and shear rates. However, in choosing a commercial viscometer a number of criteria must be considered. Of great importance is the nature of material to be tested, its viscosity, its elasticity, the temperature dependence of its viscosity, and other variables. The degree of accuracy and precision required, and whether the measurements are for quality control or research, must be considered. The viscometer must be matched to the material and process of interest; otherwise, the results may be misleading.

Viscometers may be separated into three main types: capillary, moving body, and rotational. There are other kinds, usually designed for special applications. For any given type there usually is a choice of several different instruments. The choice depends on the particular requirements of the investigator and the price range [3,7].

2.5.1 Capillary viscometers

Capillary flow measurement is a popular method for measuring viscosity; it is also the oldest. A liquid drained or its forced through a fine-bore tube, and the viscosity is determined from the measured flow, applied pressure, and tube dimensions. The basic equation is the Hagen-Poiseuille expression:

$$\eta = \frac{\pi r^4 \Delta p\, t}{8\, V L} \qquad \ldots(2.19)$$

where r is the radius of the capillary, Δp is the pressure drop through the capillary, V the volume of the liquid that flows in time t, and L the length of the capillary.

Capillary viscometers are useful for measuring precise viscosities of a large number of fluids, ranging from dilute polymer solutions to polymer melts.

Absolute viscosities are difficult to measure with capillary viscometers, but viscosities relative to some standard fluid of known viscosity, such as water, are readily determined. The viscometer is calibrated with the reference fluid, and the viscosities of other fluids relative to the reference sample are determined from their flow times [3,7].

2.5.2 Moving body viscometers

In moving body viscometers, the motion of a ball, bubble, plate, needle, or rod through a material is monitored. Falling ball viscometers are based on Stock's law, which relates the viscosity of a Newtonian fluid to the velocity of the falling sphere. If a sphere is allowed to fall freely through a fluid, it accelerates until the viscous force is exactly the same as the gravitational force.

$$\eta = \frac{2r^2 g(\rho_s - \rho_l)}{9v} \qquad \ldots(2.20)$$

where r is the radius of the sphere, ρ_s and ρ_l are the density of the sphere and the liquid respectively, and v is the velocity of the sphere.

Viscometers of the falling ball type can be used over an extremely wide viscosity range, but are usually employed for fairly viscous materials because small balls and small differences in density are needed to obtain a suitably slow rate of fall in a low viscosity fluid. The devices are limited to measurements of Newtonian fluids because no practical formula has been developed for non-Newtonian materials [3].

2.5.3 Rotational viscometers

Rotational viscometers consist of two basic parts separated by fluid being tested. The parts may be concentric cylinder (cup and bob), plates, a low angle cone and plate, or a disk paddle or rotor in cylinder. Rotation of one part against the other produces a shearing action on the fluid. The torque required to produce a given angular velocity or the angular velocity resulting from a given torque is a measure of the viscosity. Rotational viscometers are more versatile than other viscometers. They can be used with a wide range of materials because opacity, settling, and non-Newtonian behavior do not cause difficulties. Viscosities over a range of shear rates and as a function of time can be measured. Therefore, they are useful in characterizing shear thinning and time-dependant behavior. Rotational viscometers are considerably more complicated mechanically than most other viscometers.

In 1990s rotational viscometers have been developed that are either intergrated or closely interfaced with computers for operation and control of the instrument as well as for data collection, reduction, and storage. Such instruments are useful for rheological measurements and studying the structure of dispersions and formulated products. Theses new instruments are versatile, easy to use, and allow the collection, analysis, and comparison of large amounts of data in a short time [3,7].

2.5.3.1 Coaxial (concentric cylinder) viscometer

The earliest and most common type of rotational viscometer is the coaxial or concentric cylinder instrument. It consist of two cylinders, one with the other (cup and bob), keeping the specimen between them, as shown in Figure (2.17). The first practical rotational viscometer consisted of rotating cup with an inner cylinder supported by a torsion wire. In variation of this design the inner cylinder rotates [3,7].

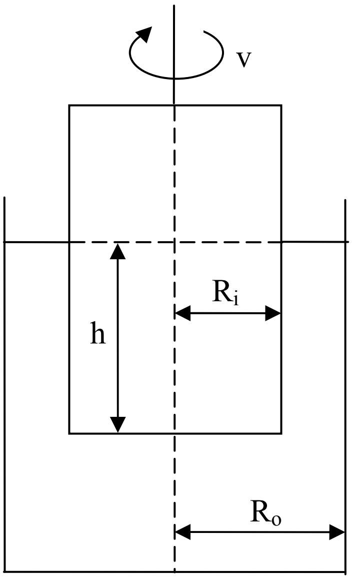


Figure (2.17) Concentric cylinder viscometer.

The relationship between viscosity, angular velocity, and torque for a Newtonian fluid in a concentric cylinder viscometer is given by Margules equation:

$$\eta = \left(\frac{M}{\Omega 4\pi h}\right)\left(\frac{1}{R_i^2} - \frac{1}{R_o^2}\right) = \frac{kM}{\Omega} \qquad \ldots(2.21)$$

Where *M* the torque on the inner cylinder, *h* the length of the inner cylinder, *Ω* the relative angular velocity of the cylinder in radius per second,

R_i the radius of inner cylinder wall, R_o the radius of the outer cylinder wall, and k an instrument constant.

Therefore, the viscosity can be determined from the torque and angular velocity. However, the viscosity is usually calculated from the shear rate and the shear stress, which can be obtained from the Margules equation, where r is any given radius:

$$\dot{\gamma} = \frac{\left(2\Omega / r^2\right)\left(R_i^{\,2} R_o^{\,2}\right)}{\left(R_o^{\,2} - R_i^{\,2}\right)} \qquad \ldots(2.22)$$

$$\tau = \frac{M}{2\,\pi\,r^2\,h} \qquad \ldots(2.23)$$

The shear rate and shear stress can be calculated for any radius r from these equations. In most cases the radius used is Ri because the shear stress and shear rate of the interest are the inner, torque-sensing cylinder. Thus:

$$\dot{\gamma} = \frac{2\,\Omega\,R_o^{\,2}}{\left(R_o^{\,2} - R_i^{\,2}\right)} \qquad \ldots(2.24)$$

$$\tau = \frac{M}{2\,\pi\,R_i^{\,2} h} \qquad \ldots(2.25)$$

The viscosity of Newtonian fluid may be determined from Margules equation or from the slope of shear stress-shear rate plot. Non-Newtonian fluids give intercepts and curves with such plots. Viscosities can be calculated, but accurate values depend one including correction factors for yield points and shear thinning, ie, shear rate correction, in the above equations [3,7,9].

2.5.3.2 Cone and Plate viscometer

In Cone and plate viscometer, Figure (2.18), a low angle (≤ 3°) cone rotates against a flat plate with the fluid sample between them. The cone-plate instrument is a simple, straightforward device that is easy to use and extremely easy to clean. It is well suited to routine work because measurements are rapid and no tedious calculations are necessary. With careful calibration and good temperature control it can also be used for research. Heated instruments can be used for melt viscosity measurements.

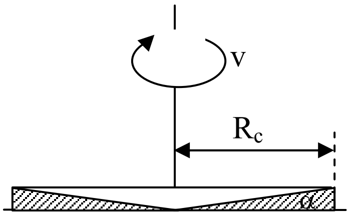


Figure (2.18) Cone-plate viscometer [3].

In most rotational viscometers the rate of shear varies with the distance from a wall or the axis of rotation. However, in cone-plate viscometer the rate of shear across the conical gap is essentially constant because the linear velocity and the gap between the cone and the plate both increase with increasing distance from the axis. No tedious correction calculation are required for non-Newtonian fluids.

The relevant equations for viscosity, shear stress, and shear rate at small angle α of Newtonian fluids are:

$$\eta = \frac{3\alpha M}{2R_c^{\ 3}} \qquad \ldots(2.26)$$

$$\tau = \frac{3M}{2\pi R_c^{\ 3}} \qquad \ldots(2.27)$$

$$\dot{\gamma} = \frac{dv}{dr} = \frac{\Omega}{\alpha} \qquad \ldots(2.28)$$

Where R_c the radius of the cone, v the linear velocity, and r the distance from the axis.

Cone-plate geometry has several advantages over concentric cylinder geometry, including smaller sample size, a homogenous shear rate, and easy conversion of data. Disadvantages include the need for precise adjustment of the gap, including resetting when the temperature is changed, specimen drying, solvent evaporation, slinging of material from the gap, and the possibility of viscous heating, particularly at high shear rates [3,7,9].

2.6 Previous Works

In this section we will focus on the recent works that studied the rheology of polymer solutions.

Song, et al. (2006) [23], studied Xanthan gum solutions for oscillatory shear flow behavior. In this study they used a strain-controlled rheometer [Advanced Rheometric Expansion System (ARES)].

Both the strain amplitude and the concentration dependencies of dynamic viscoelastic behavior were firstly reported at full length from the experimental data obtained from strain tests. Secondly, the linear viscoelastic behavior was explained in detail and the effects of angular frequency and concentration on this behavior were discussed using the well-known power-law type. Finally, a fractional derived model originally developed by Ma and Barbosa-Canovas (1996) was employed to make a quantitative description of a linear viscoelastic behavior and then the applicability of this model was examined with brief comment on its limitations.

They concluded that Xanthan gum solutions do not form a chemically cross-linked stable (strong) gel but exhibits weak gel-like behavior, begin regarded as a highly elastic liquid over a wide range of time scale. Also they concluded that a fractional derived model may be attractive means for predicting a linear viscoelastic behavior of concentrated Xanthan gum solutions. However, this model may be classified as a semi-empirical relationship because there exists no real physical meaning for the model parameters.

Tapadia and Wang (2006) [24], used a particle tracking velocimetric technique to study the rheology of non-Newtonian polymeric fluid (10 wt% 1,4-polybutadiene solution). They showed a direct evidence of nonlinear velocity profiles during simple-shear flow of an entangled polymer solution, offering a new insight into of such characteristics as stress overshoot.

They used a particle tracking velocimetry consists of sending a laser beam along the velocity gradient direction through the gap between cone and plate and video recording the illuminated moving particles over time with CCD camera facing the gap as shown in Figure (2.19).

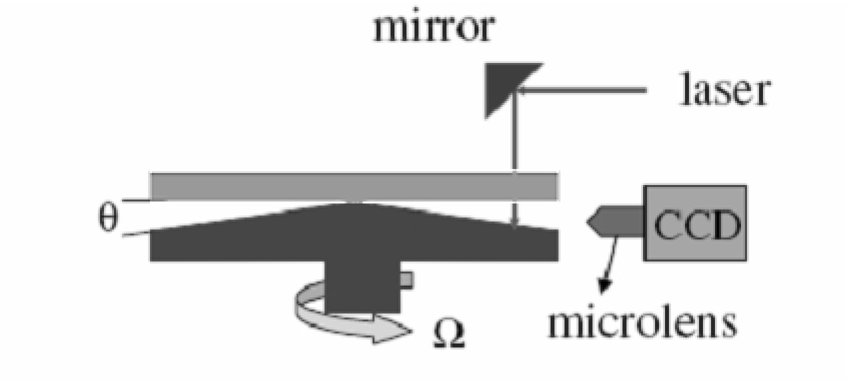
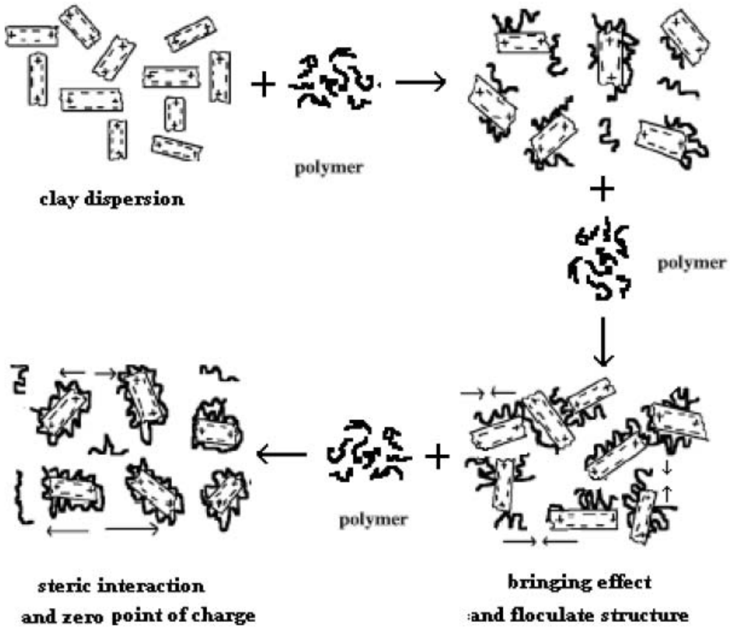


Figure (2.19) The setup of the particle tracking velocimetry [24].

İşçi, et al. (2006) [25] studied the rheology and structure of aqueous bentonite-polyvinyl alcohol dispersions. The influence of polymer on flow behavior of Balikesir, Turkey bentonite dispersion (2% w/w) was studied for non-ionic polymer, polyvinyl alcohol (PVA). In a range of $3.3\times10^{-6} - 3.3\times10^{-5}$ mol/l PVA was added to the bentonite dispersions in different concentrations and its behavior was observed on rheology parameters. The data were interpreted taking into account the interactions of colloidal clay particles, bentonitic clay concentrations, structure, and concentrations of added PVA. The particle size analysis was explained by surface orientation of PVA to the clay particles dispersed in aqueous solution. Zeta potential determination also emphasized that PVA molecules got attached on the face and edge surface of clay particles



Figure(2.20) Schematic representation of adsorption of PVA polymer on bentonite particles as a function of concentration of polymer [25].

Figure (2.20) shows a schematic representation of adsorption of PVA polymer on bentonite particles as a function of concentration of polymer. Increasing concentration of PVA results in a decrease in the zeta potential value of the bentonite dispersions. This decrease in the zeta revealed that PVA molecules attached on the net negatively charged clay particles. As the adsorbed amount increased, zeta potential reached zero point, and with further adsorption zeta potential became a positive.

Tirtaatmadja, et al. (2002) [26] studied the rheological properties of hydrophobically modified hydroxyl ethyl cellulose (hmHEC) in the presence of an ionic sodium dodecyl sulphate (SDS) surfactant.

The hmHEC used was a commercial sample of Natrosol Plus-330PA. Shear properties of the solutions were carried out in two stress-controlled rheometers, using both a cone-and-plate and Couette geometry. Both steady and dynamic oscillatory shear measurements were carried out. All measurements were carried out at 21 °C.

Hydrophobically-modified polymers have been shown to display higher solution viscosity than their unmodified analogous at the same polymer concentration and molecular weight, due to hydrophobic association of the side chain.

As illustrated in Figure (2.21), at low stress (labeled τ_1) expansion of the network occurs allowing structural rearrangement. As the stress increased (labeled τ_2) the network undergoes partial, localized fracture. At higher stress (labeled τ_3) the network is completely fractured and a major structural change occurs.

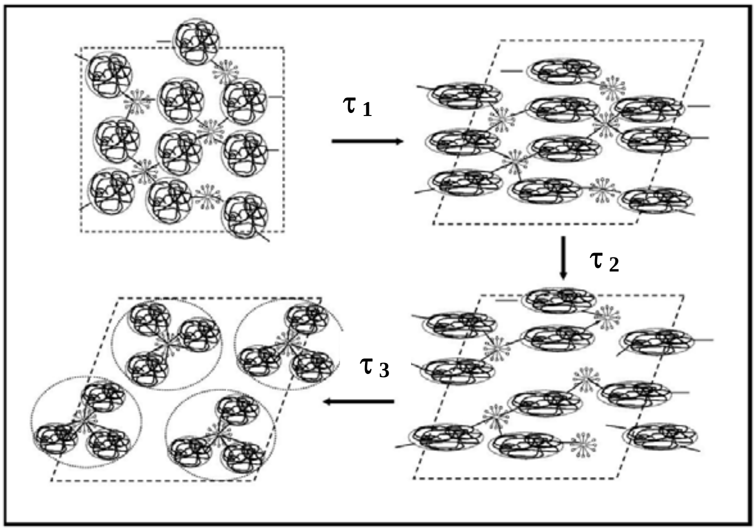


Figure (2.21) Schematic diagram of the proposed structures of polymer surfactant complexes for the solution showing shear-induced thickening, followed by structure break-up at high stresses [26]

Salami (2000) [27] studied the rheological behavior of several polymer-extended water-based drilling muds at high pressure and temperature, simulating their true working conditions in a deep oil well.

The polymers used to modify the rheological properties of the base mud were chosen to be PHPA (Partially-Hydrolyzed PolyAcrylamide), XC (Xanthan Gum) and CMC (Carboxy Methyl Cellulose). The test fluids were obtained by dissolving 1,2 and 3 grams of each of these three water-soluble polymers in 0.35 liter of base mud containing 21 grams solids (bentonite). The performance of these polymers as a rheology modifier in drilling systems was then investigated using a Fann 50 commercial viscometer, by measuring shear stress vs. shear rate (i.e. the flow curve) at pressures up to 500 psi and temperatures up to 300 °F, it was found that the temperature had a detrimental effect on the rheological properties of the test fluids while the effect of pressure on these properties was realized to be less significant (specially at pressure above 300 psi). From the stand point of the amount of polymer needed to achieve a certain properties modification, and also with regard to the effect of pressure and temperature on properties such as flow curves, it was concluded that among the three polymers studied, PHPA appeared to be the additive of choice in water-base drilling muds.

Mohammed and Halagy (2006) [28] studied the effect of rheological properties, concentrations of non-Newtonian fluids, particle shape, size and the density difference between particle and fluid on drag coefficient and settling velocity.

Two types of solid particles were used; glass spheres and irregular crushed rocks with different diameters. The settling velocity was calculated for non-Newtonian fluids which represented by power law model. Two types of polymers were used; Carboxymethyl Cellulose and Polyacrylamide.

She concluded that the rheological properties of non-Newtonian fluids have a great effect on drag coefficient, because as the fluid become far from Newtonian behavior (flow index *n* far from unity), the settling velocity will be decreased and the drag coefficient will be increased. This effect was clearly presented in laminar-slip and will decrease or vanish in turbulent and transient-slip regimes.

Leal and Oberhauser (2000) [29] wrote a status report for the progress in the development of models for non-Newtonian polymeric liquids. In their review they divided the previous works to three classes:

1. Ultradilute solutions

   In these solutions all molecular models assume that the dynamics of individual polymer molecules are independent of the presence of any other chains in the solution, both at equilibrium and in a fully deformed/stretched state.

   Depending upon the flow, the polymer may undergo a transition from random coil to a highly elongated threadlike structure of length comparable to the end-to-end contour length of the chain.

   Two examples in which there may be important technological interest in the dynamics of ultradilute polymer solutions are turbulent drag reduction and flow in porous media. It is known that exceedingly small amounts of high molecular weight polymer (a few ppm by weight) are sufficient to produce a major modification in certain turbulent flows (associated with a reduction in the apparent frictional drag at boundaries) (Berman, 1977; Den Toonder *et al*., 1997; Oliver and Bakhtiyarov, 1983; Toms, 1977) [30-33].

   Small amounts of polymer are also known to be capable of producing substantial reductions in flow rate or increases in the required pressure drop for a given flow rate for flow through a porous media (Durst *et al.*, 1981; Elata *et al.*, 1977; Haas and Durst, 1982; Rodriguez *et al.*, 1993) [34-37].

2. Dilute solutions

   In this class the solutions are sufficiently concentrated that chain interaction becomes important when the polymer is in an extended state.

   This class of fluids has been the object of extensive investigation (Baaijens *et al.*, 1995; Feng and Leal, 1997; Grillet and Shaqfeh, 1996; Yang and Khomami, 1999 [38-41].

   Because of the fact that very strong, direct effects of the polymer on the flow tend to occur in localized regions means that these flow problems are almost certainly more difficult to solve numerically than entangled systems, where the effect of the polymer on the flow is felt more or less smoothly throughout the flow domain.

3. Entangled solutions

   For the entangled systems, there is a wide range of flow conditions where the material is characterized by a high degree of chain orientation with little or no stretch. In most flows, such fluids exhibit shear thinning (a decrease in the viscosity with increase of strain rate).

   A theory that explicitly accounts for polymer entangled solutions has been proposed by Marrucci and Grizzuti (1988) (the DEMG model), and it has been further developed and analyzed by other researchers (Mead and Leal, 1995; Mead *et al.*, 1995; Pearson *et al.*, 1991) [42-45].

Chapter Three

Experimental Work

3.1 Polymers Used

All polymers studied in this investigation are water soluble and used in industries as a rheology control additive (rheology modifiers). Five polymers are used in this study, these are: XC-polymer, Carboxymethyl cellulose (two types), Hydroxyethyl cellulose and Polyvinyl alcohol, as follow:

1. The XC polymer used in this study is a commercially available product supplied from Yongkang Rigchina Group Co. (China).
2. The HEC used in this study is a commercially available product type Cellosize QP 4400H, supplied from DOW Chemical Company (USA).
3. Two commercial products of CMC have been used in this study. The first is supplied from Qingdao Great Chemical Inc. (China), and the second is supplied from Denkim Denizli Kimya A.S. (Turkey).
4. The PVA used in this study is a commercially available product type C-17GP, supplied from Shin Etsu Chem. Co. Ltd. (Japan).

3.2 Sets of Experiments

55 experiments were performed to study the rheological properties of the aqueous solutions of polymers used in this study. Experiments were performed at 30 °C (± 1 °C). List of experiments is shown in Table (3.1).

Table (3.1) List of Experiments.

Exp.No.	Polymer	Conc.(g/l)
1	XC	4
2	XC	8
3	XC	12
4	XC	16
5	XC	20
6	XC	24
7	XC	32
8	XC	40
9	HEC	4
10	HEC	8
11	HEC	12
12	HEC	16
13	HEC	20
14	HEC	24
15	HEC	32
16	HEC	40
17	HEC	48
18	HEC	56
19	HEC	64
20	HEC	72
21	CMC-1	4
22	CMC-1	8
23	CMC-1	12
24	CMC-1	16
25	CMC-1	20
26	CMC-1	24
27	CMC-1	32
28	CMC-1	40
29	CMC-1	48
30	CMC-1	56
31	CMC-1	64
32	CMC-1	72
33	CMC-2	4
34	CMC-2	8
35	CMC-2	12
36	CMC-2	16
37	CMC-2	20
38	CMC-2	24
39	CMC-2	32
40	CMC-2	40
41	CMC-2	48
42	CMC-2	56
43	CMC-2	64
44	PVA	4
45	PVA	8
45	PVA	12
47	PVA	16
48	PVA	20
49	PVA	24
50	PVA	32
51	PVA	40
52	PVA	48
53	PVA	56
54	PVA	64
55	PVA	72

3.3 Equipments Used

The main equipments used in this study are:

1. Fann VG-Viscometer, Model 35A (Figure (3.1)).

2. Hamilton Beach mixer and cup (Figure (3.2)).

3. Electronic balance.

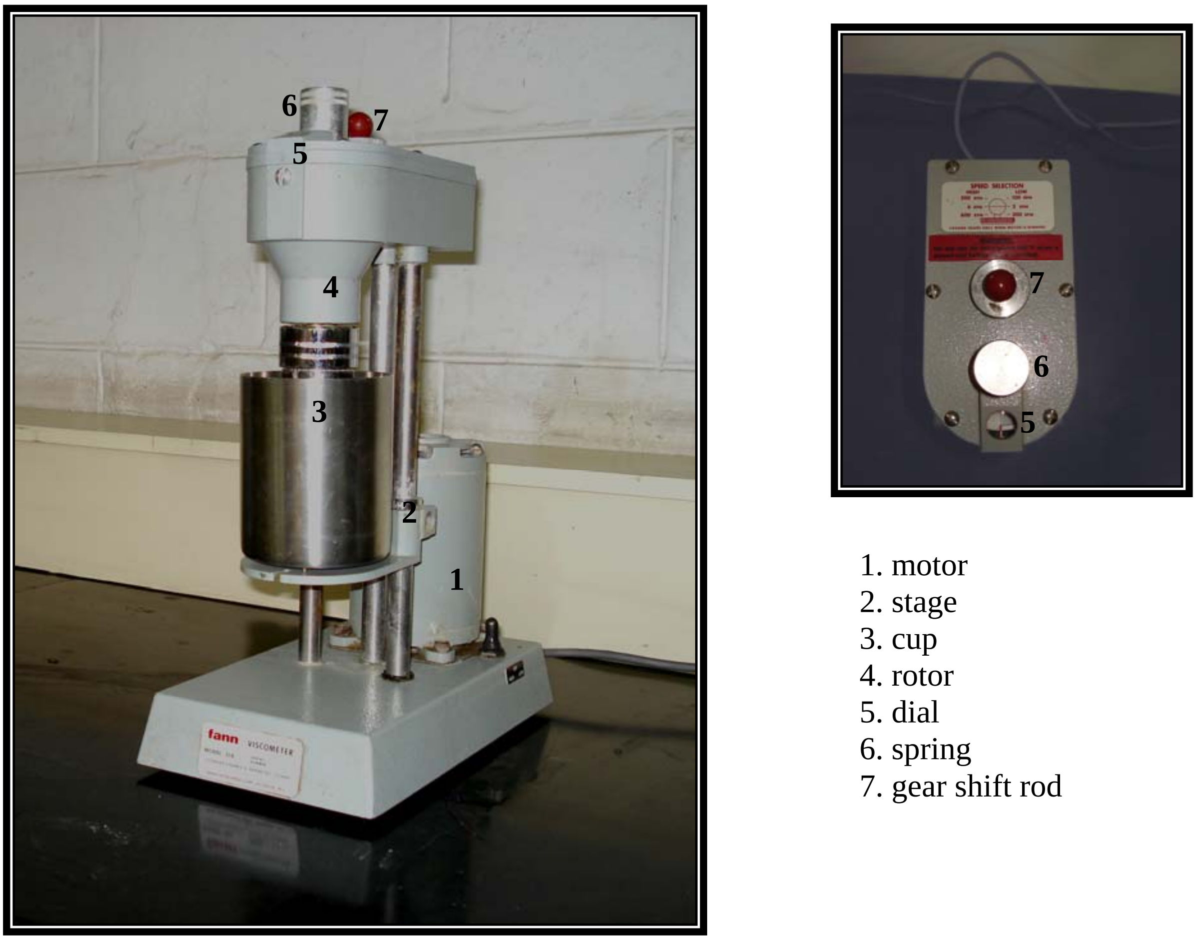
4. Drying oven.

5. Microwave oven.

6. Hot plate heater.

7. Thermometer (0 – 200 °C)

8. Stop watch.



1. motor
2. stage
3. cup
4. rotor
5. dial
6. spring
7. gear shift rod

Figure (3.1) Fann VG-Viscometer, Model 35A.

Figure (3.2) Hamilton Beach mixer and cup.

3.4 Viscometer

The Fann viscometer model 35 is a direct reading instrument which has six speeds: 600, 300, 200, 100, 6 and 3 rpm. It is a Couette coaxial cylinder rotational viscometer.

This instrument is a form of concentric cylinder viscometer that enables the variation of sheering stress with shear rate to be observed. The essential elements are shown in Figure (3.3). A bob suspended from a spring hangs concentrically in an outer cylinder. The assembly is lowered to a prescribed mark in a cup of solution, and the outer cylinder is rotated at a constant speed. The viscous drag of the solution turn the bob until it is balanced by the torque in the spring. The deflection of the bob is read from a calibrated dial on the top of the instrument, which thus provided a measure of the shear stress at the surface of the bob [46].

This instrument has been designed so that viscosity in centipoise of a Newtonian fluid is indicated on the dial with the standard rotor, bob, and torsion spring operating at 300 rpm. Viscosities at other test speeds may be measured by using multipliers of the dial reading [47].

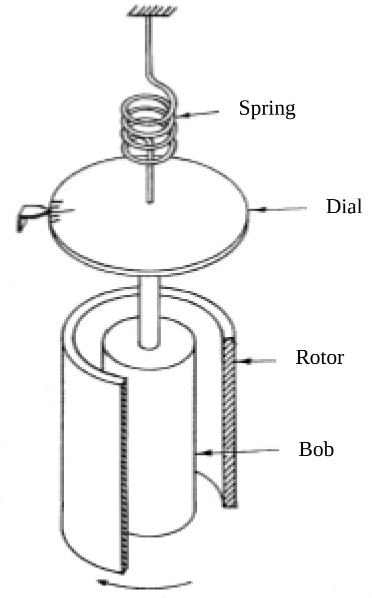


Figure (3.3) The essential elements of rotational viscometer [47].

3.4.1 Calibration of viscometer

This procedure is used for calibration using only Newtonian certified calibration fluids. Fann calibration fluids are available in nominal 20, 50, 100, 200 and 500 cP. All are traceable to ASTM standards and each bottle of fluid is furnished with a viscosity temperature chart [46].

1. The instrument must be clean before immersing the rotor and bob into the calibration fluid. If necessary the rotor is removed and the bob, bobshaft, and rotor thoroughly cleaned.

2. The sample cup was filled to the scribed line with the calibration fluid and placed it on the instrument stage. The stage was elevated so that the rotor was immersed to the proper immersion depth.

3. A thermometer was placed into the sample until the bob touches the bottom and then secured it to the side of the viscometer to prevent breakage.

4. The instrument was operated at 300 rpm for three minutes. This will equalize the temperature of the bob, rotor and the fluid.

5. The dial was read at 300 rpm and 600 rpm. These numbers were recorded, and the temperature from the thermometer to the nearest 0.1 °C.

The viscosity from the temperature chart at the recorded temperature should be within ± 2 cP of the 300 rpm reading. Twice the cP viscosity from the chart should be within ± 3 of the 600 rpm reading. If zero, 300 and 600 rpm do not fall in a straight line, probably either the rotor, bob or bobshaft is bend. Points at 100 and 200 rpm can be plotted if verification is needed [46].

3.5 Preparation of Polymer Solution

Polymer solutions must be prepared with care. Special effort should be expended to ensure complete, homogeneous dissolution [48].

3.5.1 Preparation of CMC, HEC and XC polymer solutions

The method for preparing a sample of polymeric solution at a certain concentration was as follow:

1. 500 ml of distilled water was measured in a volumetric flask and placed in the Hamilton Beach cup.
2. A previously dried polymer powder was weighted to the nearest 0.001g using electronic balance.
3. The polymer lightly sprinkled into the water while stirring continuously.
4. Stirring continued for one hour to ensure completely polymer dissolution.
5. The prepared solution was poured into a properly labeled bottle and sealed.
6. The prepared solution was kept at rest at room temperature for 24 hr prior to conducting the rheological measurements.

3.5.2 Preparation of PVA solution

There are two methods for preparing aqueous solution of polyvinyl alcohol, the conventional heating method and the microwave heating method.

The microwave oven method is the preferred method for preparing the PVA solution [20,49], so it was considered in this investigation as follow:

1. Dry PVA powder was weighted to the nearest 0.001g using electronic balance.
2. The polymer was added to 500 ml of distilled water in a Pyrex beaker with stirring.
3. The beaker was covered with microwave plastic warp and placed in a microwave oven.

4. The microwave was turned on high for three minutes.

5. The solution was stirred and heated for an additional three minutes.

6. The prepared solution was allowed to cool, and then poured into a properly labeled bottle and sealed.

7. The prepared solution was kept at rest at room temperature for 24 hr prior to conducting the rheological measurements

3.6 Rheological Measurements

The procedure for measuring the rheological properties of polymer solutions, using the Fann viscometer model 35 was as follow:

1. The instrument was cleaned using distilled water before immersing the rotor and bob into the polymer solution. If necessary, the rotor was removed and the bob, bob shaft and the rotor was cleaned thoroughly.

2. The sample cup was filled with polymer solution to the scribed line, and the cup was placed on the instrument stage. The instrument stage was elevated so that the rotor was immersed to the proper immersion depth.

3. The instrument was operated at 300 rpm for three minutes to equalize the temperature of the bob, rotor and polymer solution.

4. The instrument speed was switched to 600 rpm and the dial reading was recorded.

5. Step 4 was repeated for 300, 200, 100, 6 and 3 rpm.

Chapter Four

Results and Discussion

In this chapter we *first* study the flow curve of each experiment and find the best model that fits the experimental results and calculate its parameters.

Secondly, the effects of polymer concentration on flow model parameter and on solution viscosity are investigated.

Finally, a comparison between different polymer solution systems used in this work is done.

4.1 Experimental Results

The Fann, model 35, viscometer has been designed so that the shear rate measured in rpm and shear stress in dial reading unit. To convert the shear rate and shear stress to SI units, the following conversion equation was used [46]:

$$\text{Shear rate, } \dot{\gamma} \text{ (1/s)} = k_3\, N \text{ (rpm)} \qquad \ldots(4.1)$$

$$\text{Shear stress, } \tau \text{ (Pa)} = 0.1\, k_1\, k_2\, \theta \qquad \ldots(4.2)$$

in which:

$k_1 = 386$

$k_2 = 0.01323$

$k_3 = 1.7023$

θ = dial reading

Sample of selected experimental results are presented in Figures (4.1) to (4.5), which are a plot of shear stress versus shear rate. In each figure two curves were drawn, one at the lower polymer concentration used, and the other at the maximum polymer concentration which can be measured in the Fann viscometer instrument.

The flow curves of all experiments are shown in Appendix (A).

From these figures, one can notice that the shear stress increase with increasing shear rate in a non-linear shape. The curves are bending down.
As polymer concentration increases, the values of the shear stresses increased.

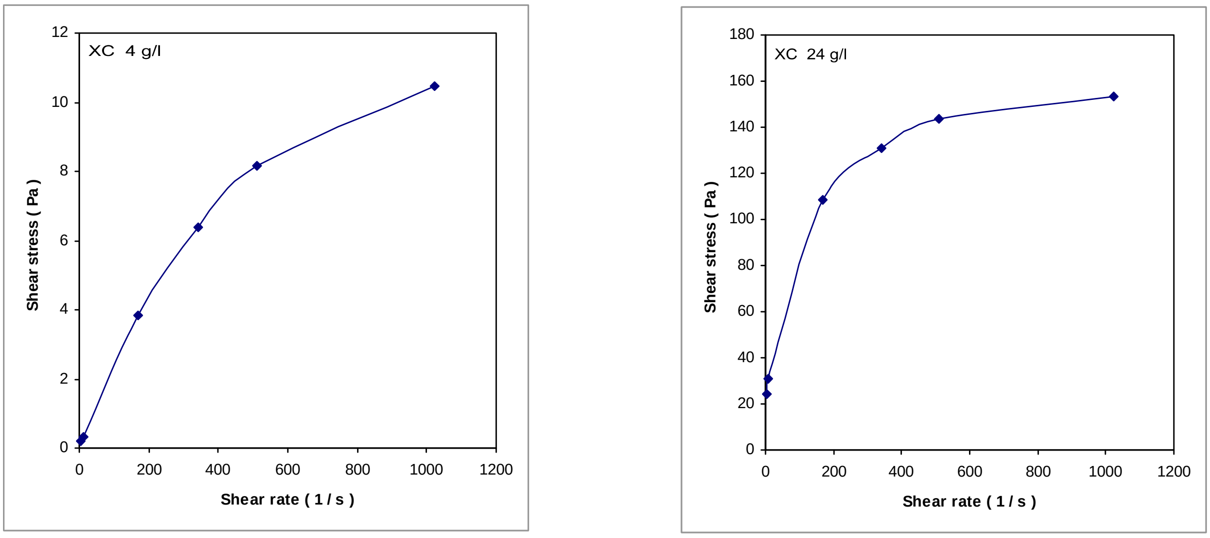


Figure (4.1) Flow curves for XC polymer solution at concentration 4 and 24 g/l.

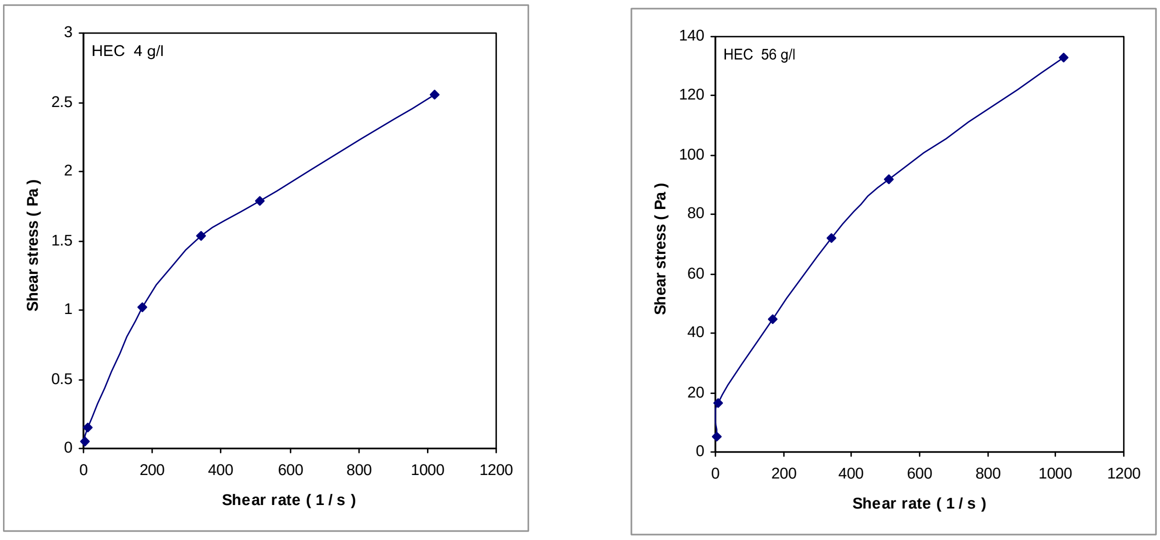


Figure (4.2) Flow curves for HEC solution at concentration 4 and 56 g/l.

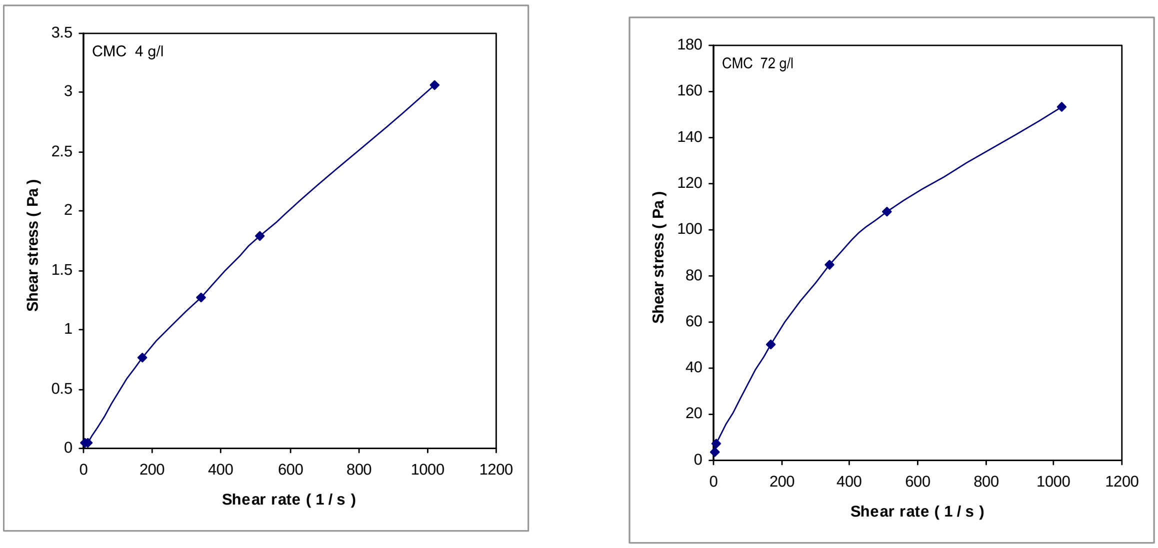


Figure (4.3) Flow curves for CMC-1 solution at concentration 4 and 72 g/l.

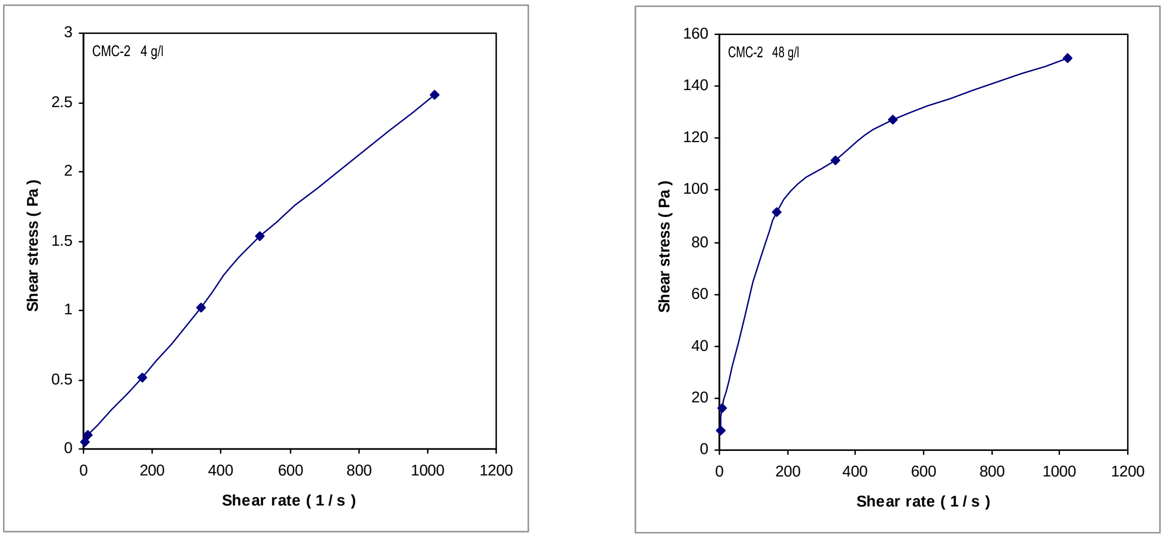


Figure (4.4) Flow curves for CMC-2 solution at concentration 4 and 48 g/l.

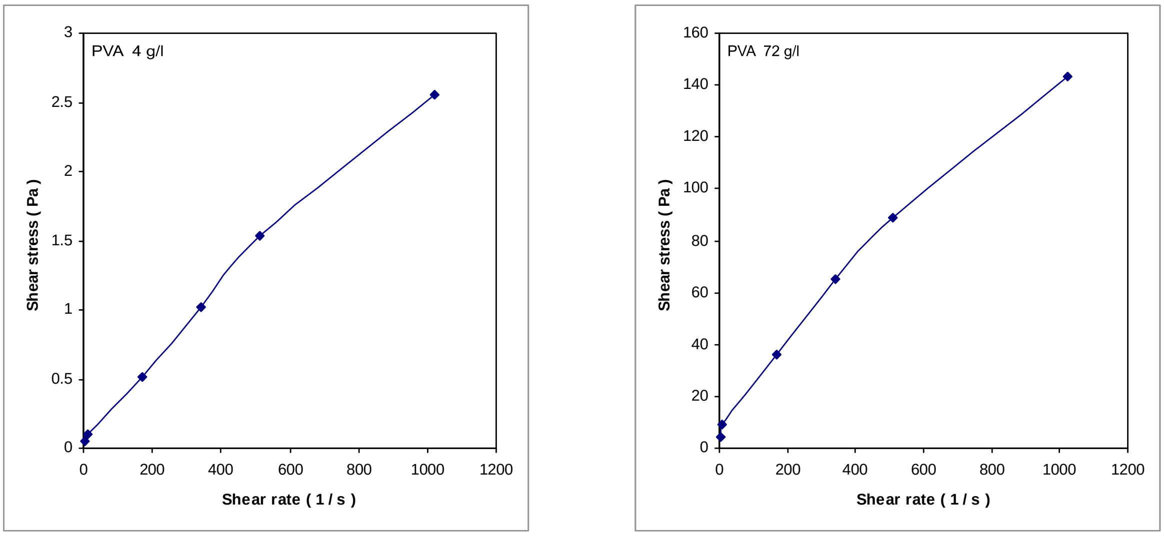


Figure (4.5) Flow curves for PVA solution at concentration 4 and 72 g/l.

4.2 Flow Model Selection

The selection of the flow model that best fit the rheological behavior is useful for treating experimental data or for describing flow behavior.

In this work a method is used proposed by Faith A. Morrison (2005) is used [50]. This method uses the Solver Add-in in Microsoft Excel® to optimize the solution.

The basic outlines of this method include:

- We begin by arranging the experimental data in the Excel spreadsheet. We will use two column, one for shear rate and one for shear stress.
- We create a column that has a predicted value of shear stress calculated from a considered flow model. Since we do not know the values of any of our model parameters, we will start with some guesses.
- We now need to create a new column for the square of the deviation between the actual shear stress and the predicted value. We add up all the values in the error column and put that value in a cell.
- The Solver function in the Excel® is set up to minimize the Error cell mentioned above.
  Solver will replace our initial guesses with optimized values.
- The Solver allow us to put constrains on the ways in which it manipulate the cells it is changing. For our work we know that none of the model parameters may be negative, so we put this as a constraint.

The results for using the Add-in in Microsoft Excel for the XC polymer solutions are shown in Table (4.1). The results for other polymer solutions are shown in Appendix (B).

From these tables, one can conclude that the Power Law model best fits the experimental results. So this model will be considered in the following sections.

The Power Law with Yield model (equation (2.10)) gives the same results as the Power Law model, the Solver replace the guess value of the yield point and set it equal to zero, so this model became the same as the Power Law model.

Also the Robertson-Stiff model (equation (2.12)) gives the same results, because the Solver set the parameter C equal to zero.

Figures (4.6) and (4.7) illustrate the results of using the Solver Add-in in Microsoft Excel for XC polymer solutions at 20 and 24 g/l respectively.

Table(4.1) Model selection for XC Polymer solutions using Add-in in Microsoft Excel.

Exp. No.	**Conc. (g /l)**	**Sum of Square Error**					
		Newtonian Eqn.(2.4)	**Bingham Eqn.(2.8)**	**Power Law Eqn.(2.9)**	**With Yield Eqn.(2.10)**	**Casson Eqn.(2.11)**	**Robertson Eqn.(2.12)**
1	4	0.997	0.331	0.130	0.130	0.252	0.130
2	8	1.248	0.253	0.063	0.063	0.163	0.063
3	12	1.705	0.476	0.081	0.081	0.301	0.081
4	16	2.087	0.597	0.106	0.106	0.376	0.106
5	20	2.226	0.453	0.048	0.048	0.248	0.048
6	24	2.641	0.523	0.065	0.065	0.286	0.065

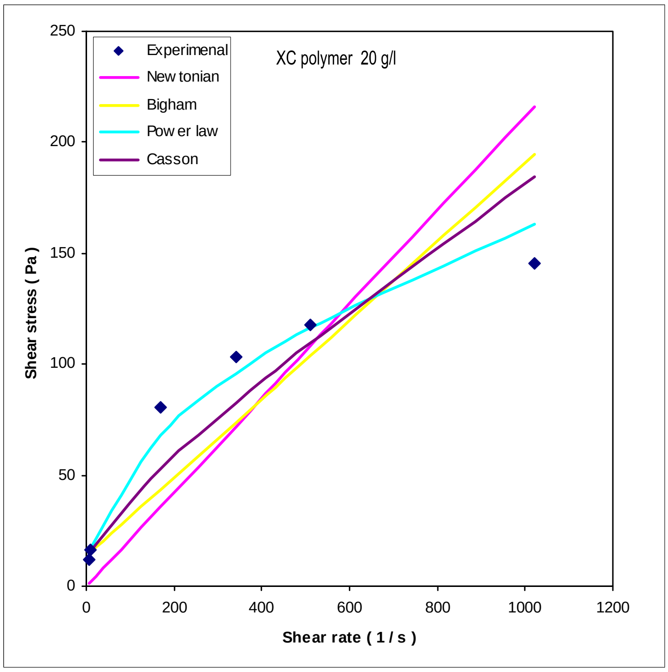


Figure (4.6) Experimental results and flow models representation For 20 g/l XC polymer solution.

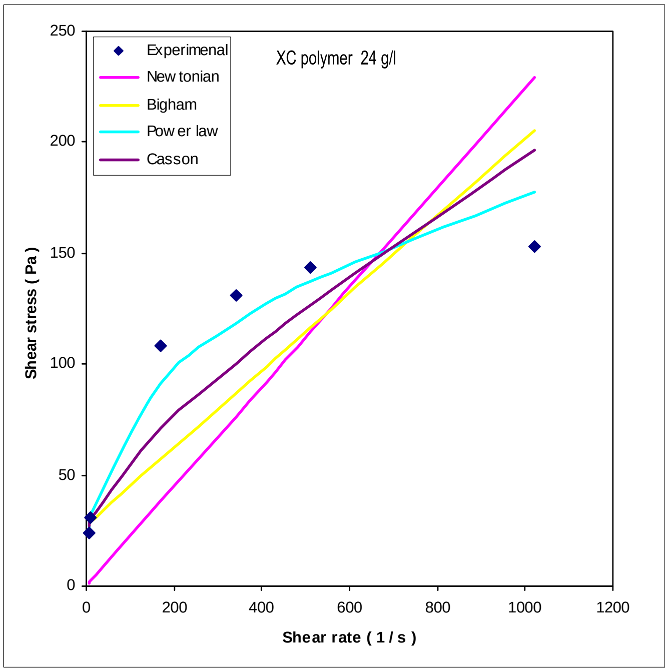


Figure (4.7) Experimental results and flow models representation For 24 g/l XC polymer solution.

4.3 The Power Law Model

To determine the values of the power law parameters, namely, flow behavior index (n) and consistency index (k), the shear stress versus shear rate are plotted on logarithmic scale.

The power law index (n) is the slope of the line, while the power law consistency is the intercept of the line with shear stress equal to one.

Selected flow curves, for lower and upper polymer concentration on logarithmic scale are shown in Figures (4.8) to (4.12).

The values of n and k , with the correlation coefficients of the best fit line (R^2) for all experiments are presented in Table (4.3). The results for Experiments no. 7,8,19,20, 42 and 43 are ignored because the shear stress readings at high shear rates are out of the scale range for the Fann viscometer.

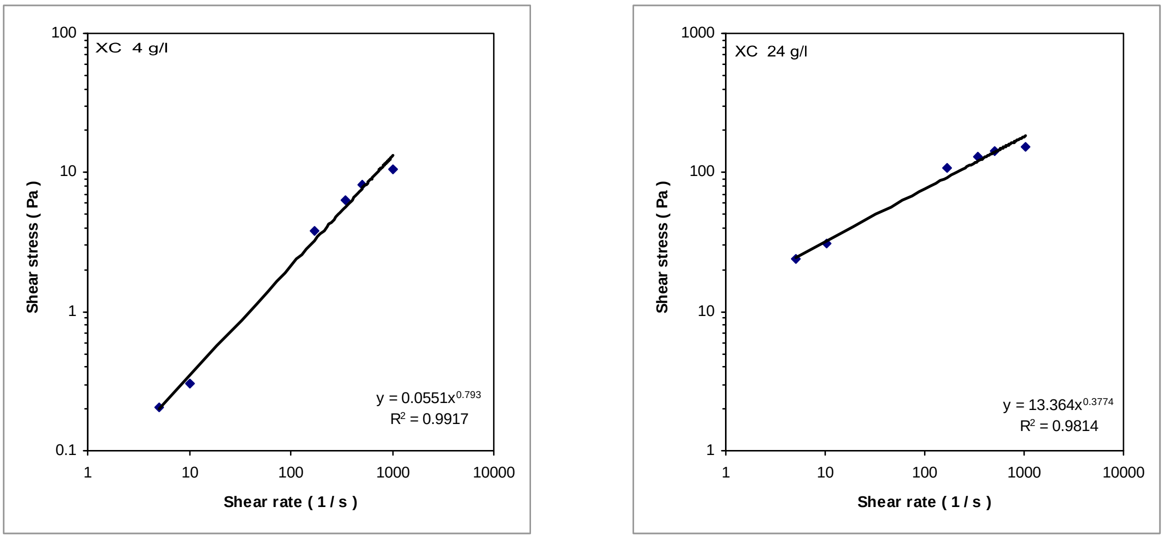


Figure (4.8) Flow curves for XC polymer solution at concentration 4 and 24 g/l.

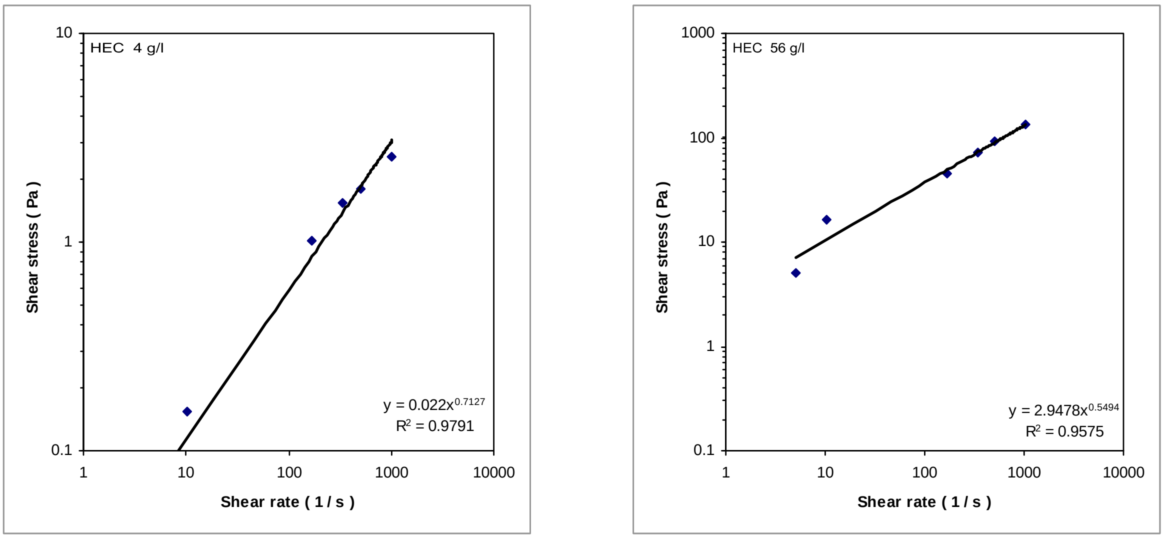


Figure (4.9) Flow curves for HEC solution at concentration 4 and 56 g/l.

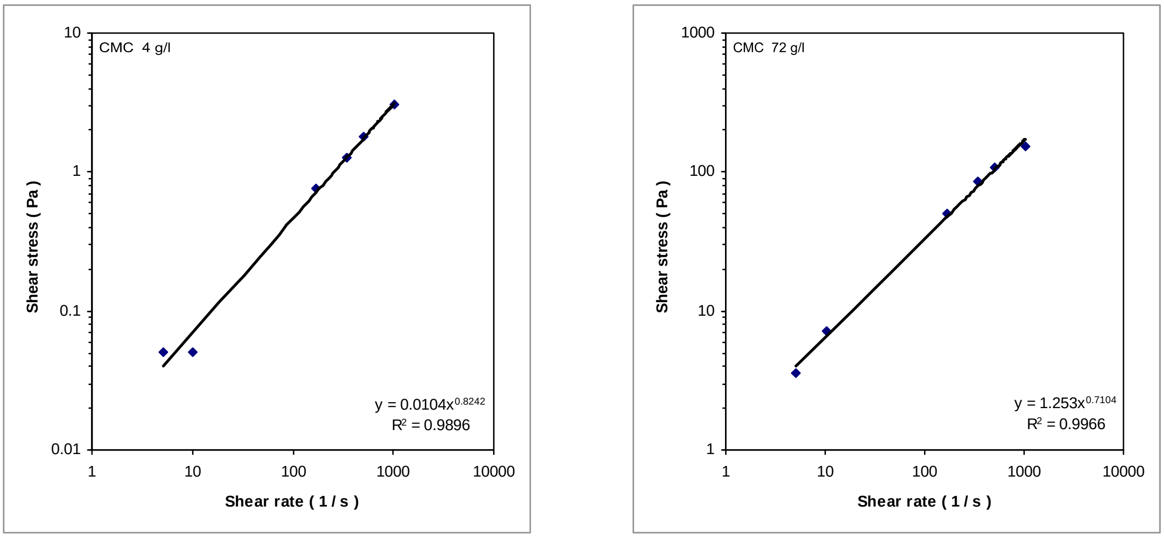


Figure (4.10) Flow curves for CMC-1 solution at concentration 4 and 72 g/l.

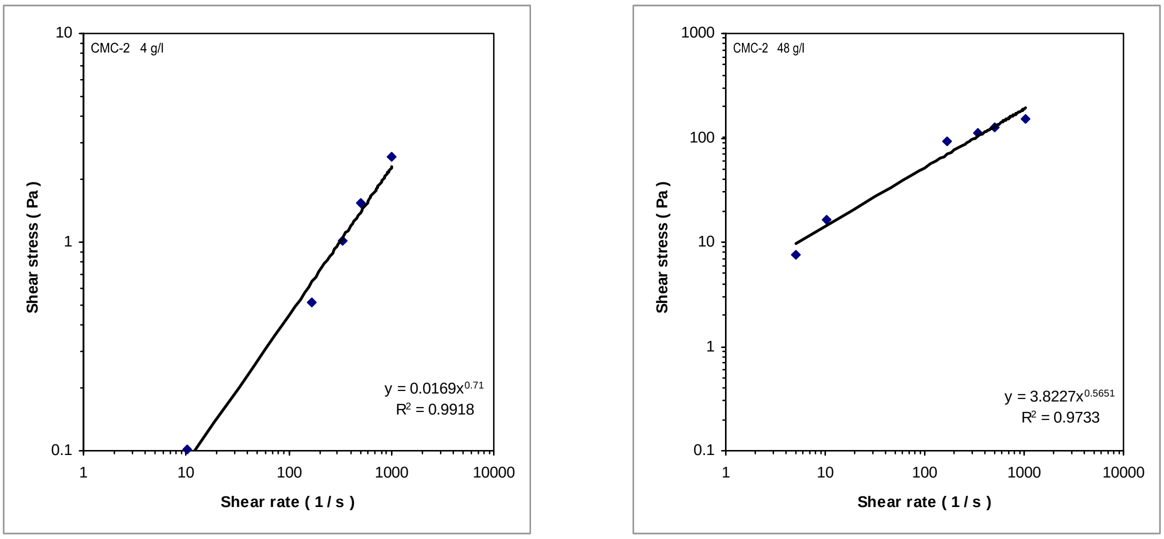


Figure (4.11) Flow curves for CMC-2 solution at concentration 4 and 48 g/l.

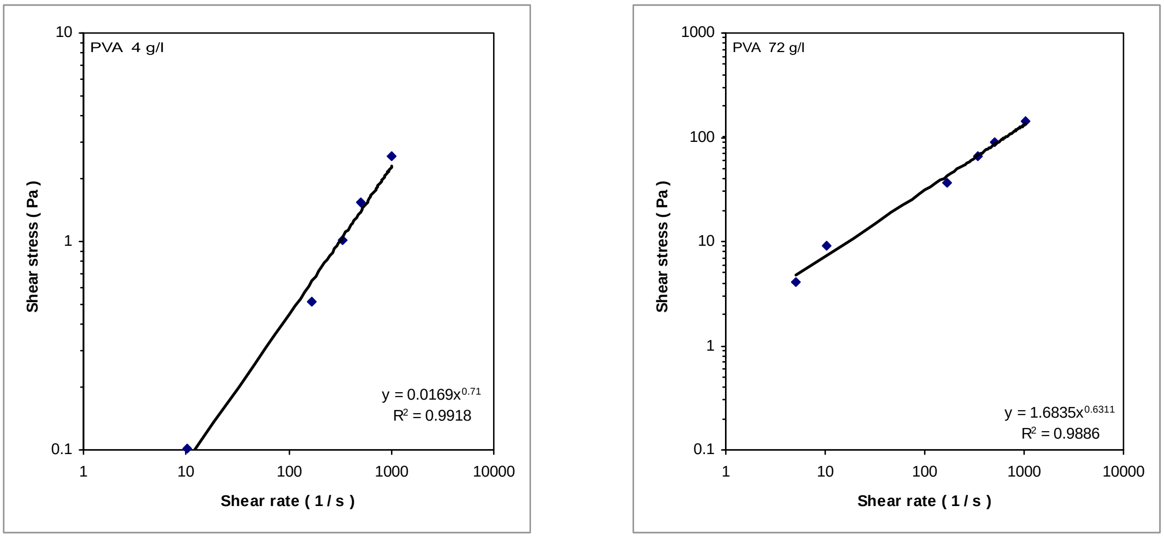


Figure (4.12) Flow curves for PVA solution at concentration 4 and 72 g/l.

Table (4.2) Flow behavior index (n) and consistency index (k).

Pol-ymer	Conc g/l	n	k	R^2
XC	4	0.7930	0.0551	0.9917
XC	8	0.7113	0.2253	0.9949
XC	12	0.6479	0.7762	0.9923
XC	16	0.5684	2.6841	0.9857
XC	20	0.4904	5.5641	0.9913
XC	24	0.3774	13.364	0.9814
XC	32	-	-	-
XC	40	-	-	-
HEC	4	0.7127	0.022	0.9791
HEC	8	0.6272	0.0692	0.9817
HEC	12	0.6334	0.0991	0.9825
HEC	16	0.6273	0.1287	0.9906
HEC	20	0.6260	0.2135	0.9639
HEC	24	0.5973	0.3637	0.9841
HEC	32	0.5958	0.4924	0.985
HEC	40	0.5852	0.6978	0.9913
HEC	48	0.5497	1.8832	0.9987
HEC	56	0.5494	2.947	0.9575
HEC	64	-	-	-
HEC	72	-	-	-
CMC-1	4	0.8242	0.0104	0.9896
CMC-1	8	0.7807	0.0152	0.9982
CMC-1	12	0.6904	0.0300	0.9848
CMC-1	16	0.7362	0.0354	0.9868
CMC-1	20	0.6679	0.0656	0.9776
CMC-1	24	0.6935	0.086	0.9871
CMC-1	32	0.7316	0.1192	0.9868
CMC-1	40	0.7354	0.1584	0.9883
CMC-1	48	0.7255	0.3024	0.9975
CMC-1	56	0.7223	0.5366	0.9910
CMC-1	64	0.7166	0.8617	0.9929
CMC-1	72	0.7104	1.2530	0.9966
CMC-2	4	0.7100	0.0169	0.9918
CMC-2	8	0.7032	0.0208	0.9791
CMC-2	12	0.6725	0.0363	0.9877
CMC-2	16	0.6387	0.096	0.9851
CMC-2	20	0.6556	0.182	0.9725
CMC-2	24	0.6564	0.3520	0.9909
CMC-2	32	0.6519	0.7558	0.9829
CMC-2	40	0.6000	2.1249	0.9847
CMC-2	48	0.5651	3.8227	0.9733
CMC-2	56	-	-	-
CMC-2	64	-	-	-
PVA	4	0.7100	0.0169	0.9918
PVA	8	0.6645	0.0335	0.9991
PVA	12	0.6879	0.0316	0.9983
PVA	16	0.6835	0.0362	0.9954
PVA	20	0.6671	0.0605	0.9942
PVA	24	0.6606	0.0930	0.9903
PVA	32	0.6947	0.1199	0.9598
PVA	40	0.6575	0.1867	0.9891
PVA	48	0.6771	0.3470	0.9746
PVA	56	0.6437	0.6234	0.9903
PVA	64	0.6196	1.4383	0.9809
PVA	72	0.6311	1.6835	0.9886

4.4 Effect of Polymer Concentration on Flow Curves

The effect of polymer concentration on flow curves are shown in Figures (4.13) to (4.17).

From these figures one can notice that at low polymer concentration the flow curves are almost linear because they are not far from Newtonian behavior. As the concentration increased the values of shear stresses increased and these fluids become far from Newtonian behavior.

At low polymer concentrations, the flow curves are less sensitive to increase in concentration and the flow curves are close. As polymer concentration increased the flow curves become more sensitive and the curves apart.

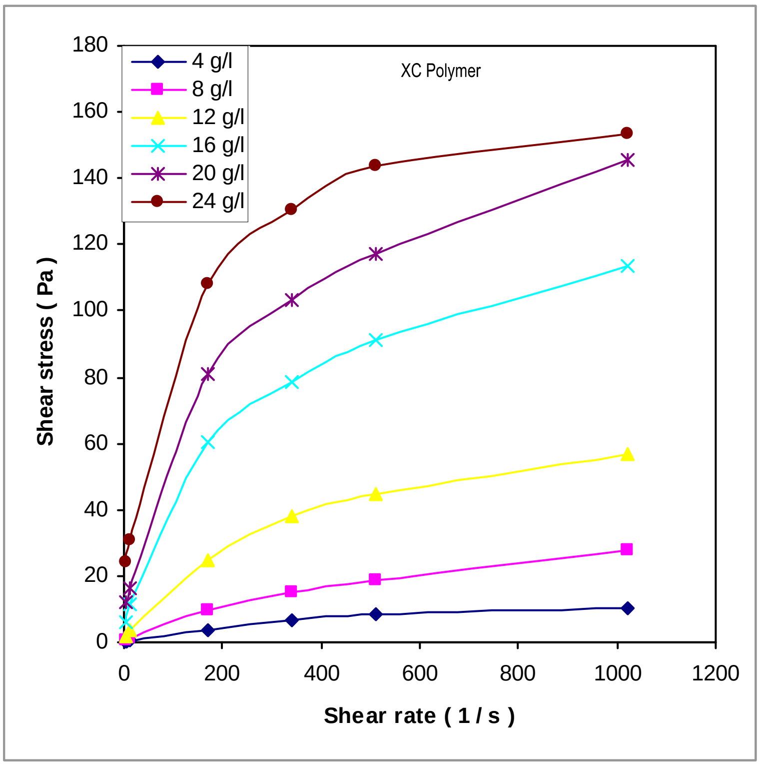


Figure (4.13) Effect of XC polymer concentration on flow curves.

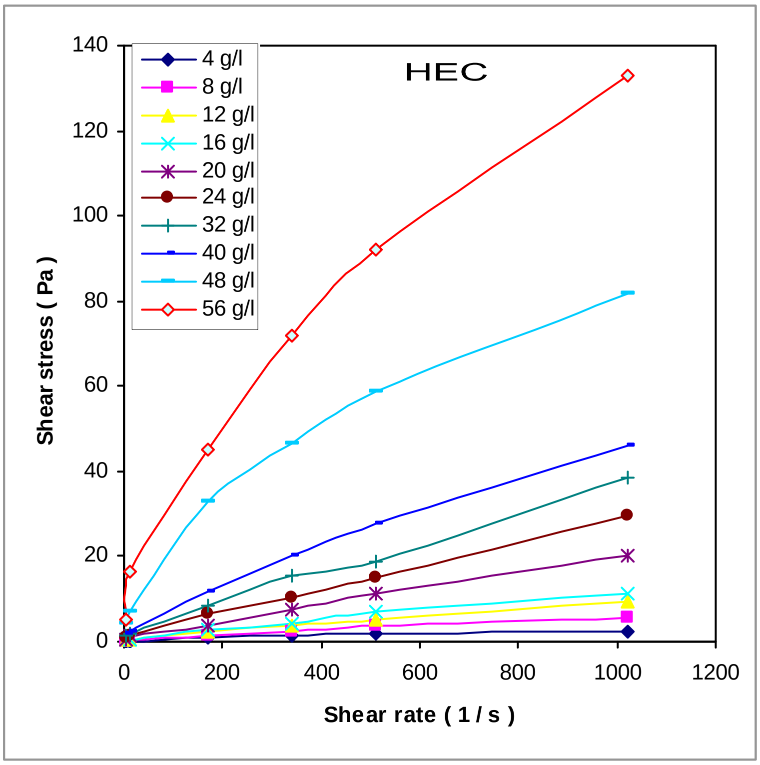


Figure (4.14) Effect of HEC concentration on flow curves.

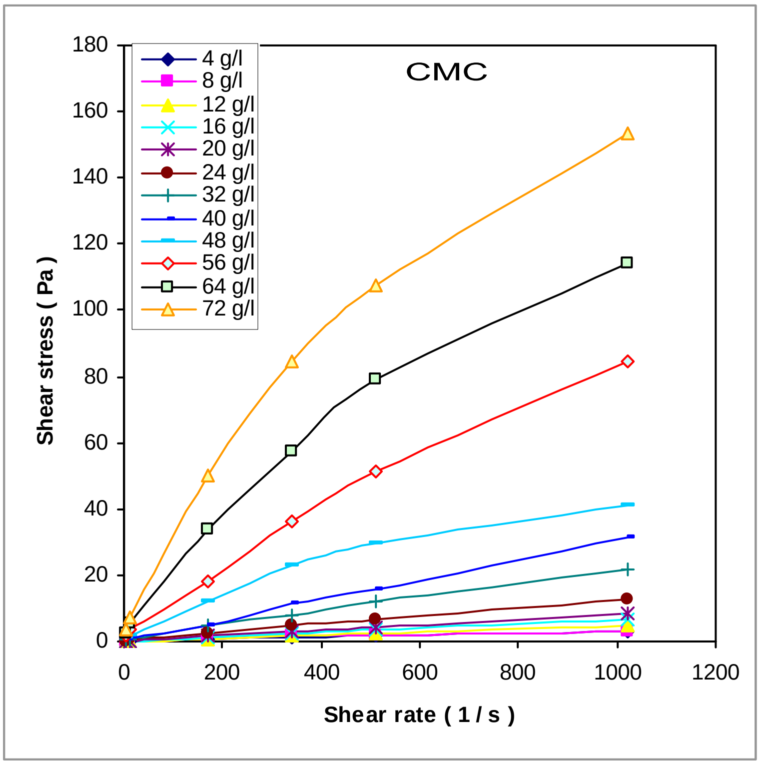


Figure (4.15) Effect of CMC-1 concentration on flow curves.

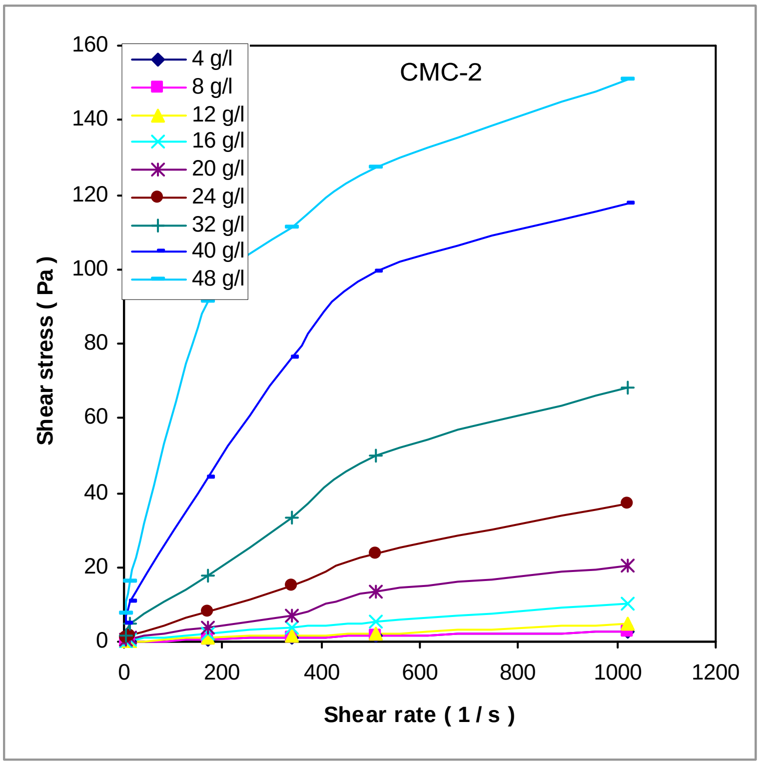


Figure (4.16) Effect of CMC-2 concentration on flow curves.

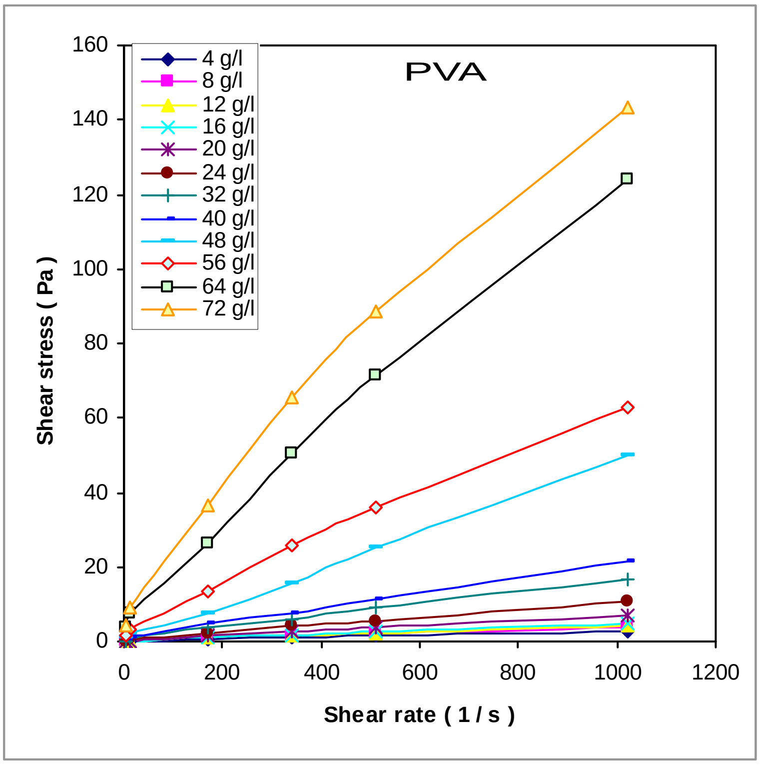


Figure (4.17) Effect of PVA concentration on flow curves.

The effects of polymer concentration on the flow behavior index (n) for all polymer solution used are shown in Figure (4.18).

From this figure one can conclude that as the polymer concentration increased, n decreased. This behavior reflect the fact that as the polymer concentration increases the solution become more non-Newtonian.

Equations that describe the effect of polymer concentration on the flow behavior index can be presented in a linear form as shown in equations below:

$$n_{XC} = - 0.02030\ C_{XC} + 0.8791 \qquad R^2 = 0.9938 \qquad \ldots(4.3)$$

$$n_{HEC} = - 0.00240\ C_{HEC} + 0.6737 \qquad R^2 = 0.8081 \qquad \ldots(4.4)$$

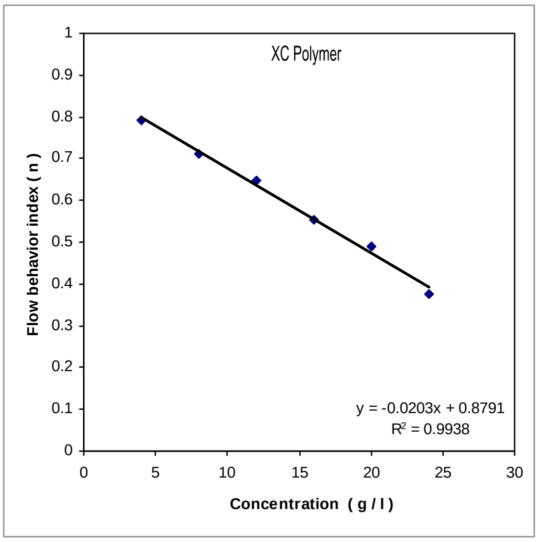
$$n_{CMC1} = - 0.0006\ C_{CMC1} + 0.7482 \qquad R^2 = 0.1150 \qquad \ldots(4.5)$$

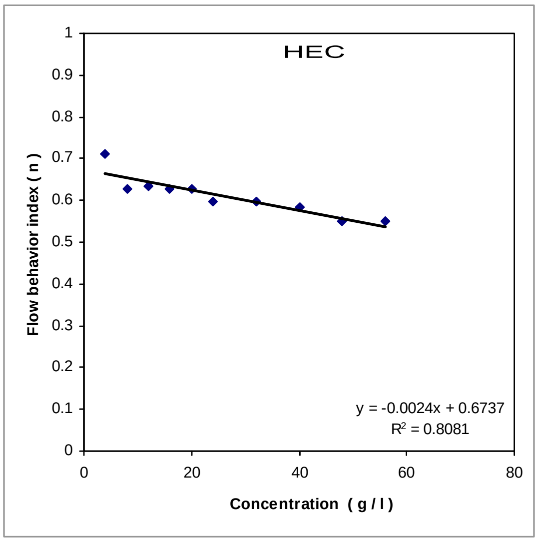
$$n_{CMC2} = - 0.0029\ C_{CMC2} + 0.7157 \qquad R^2 = 0.8673 \qquad \ldots(4.6)$$

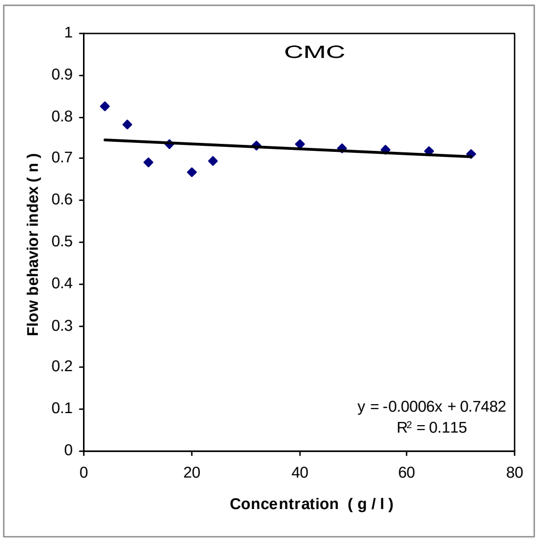
$$n_{PVA} = - 0.0009\ C_{PVA} + 0.6964 \qquad R^2 = 0.6165 \qquad \ldots(4.7)$$

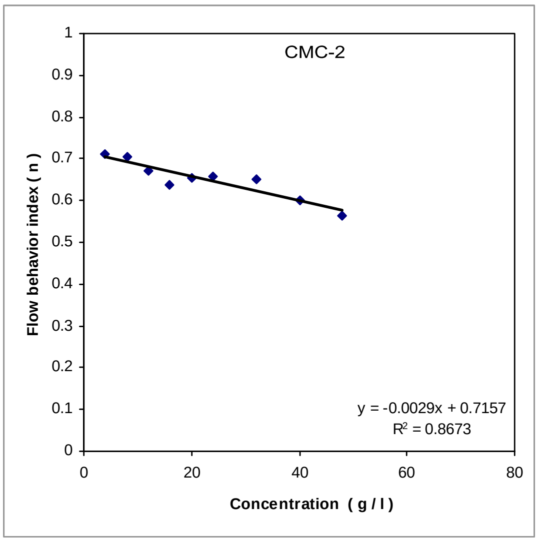
From the above equations and from Figure (4.18) we can notice that n for XC polymer is more effected by concentration than other polymer used in this study. While PVA and CMC (type 1) is less effected than other. And we can conclude that, in the range of polymer concentrations used in this study, n affected by concentration in the order:

$$n_{XC} > n_{CMC2} > n_{HEC} > n_{CMC1} > n_{PVA}$$









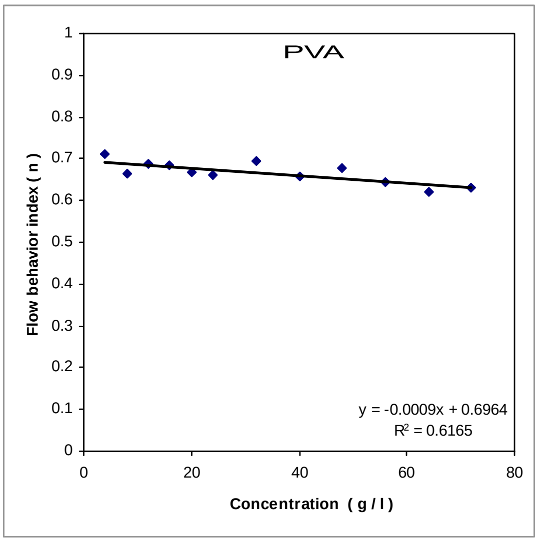


Figure (4.18)

Effect of polymer concentration on flow behavior index

The effects of polymer concentration on the consistency index (k) for all polymer solution used are shown in Figure (4.19).

From this figure one can conclude that as the polymer concentration increased, k increased. This behavior reflect the fact that as the polymer concentration increases the solution become more thicker.

Equations that describe the effect of polymer concentration on the power law consistency can be presented in an exponent form as shown in equations below:

$$k_{XC} = 0.0243\, e^{0.2743\, C} \qquad R^2 = 0.9837 \qquad \ldots(4.8)$$

$$k_{HEC} = 0.0310\, e^{0.0845\, C} \qquad R^2 = 0.9581 \qquad \ldots(4.9)$$

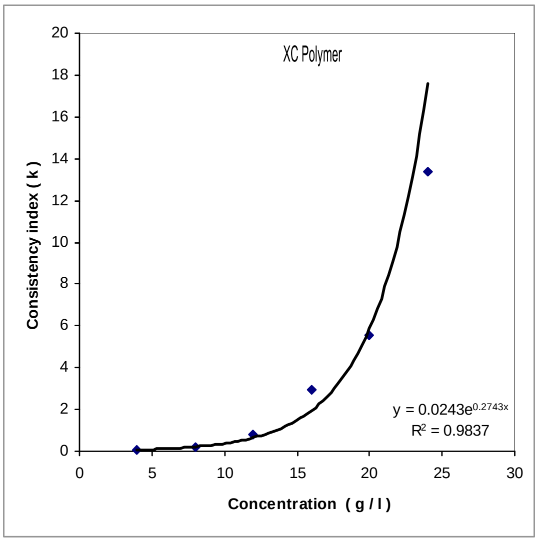
$$k_{CMC1} = 0.0119\, e^{0.0674\, C} \qquad R^2 = 0.9776 \qquad \ldots(4.10)$$

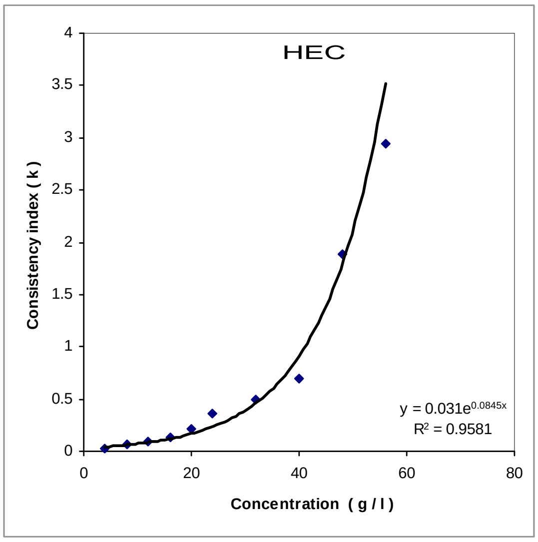
$$k_{CMC2} = 0.0101\, e^{0.1316\, C} \qquad R^2 = 0.9805 \qquad \ldots(4.11)$$

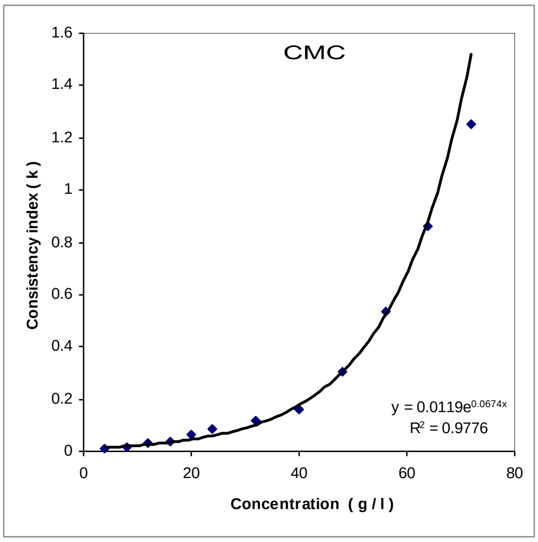
$$k_{PVA} = 0.0149\, e^{0.0672\, C} \qquad R^2 = 0.9883 \qquad \ldots(4.12)$$

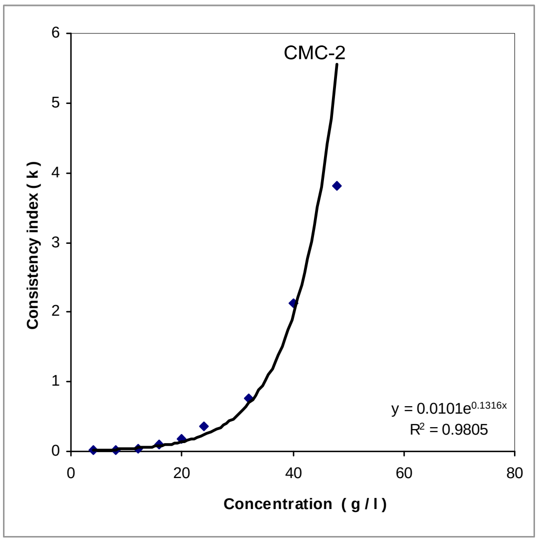
Also from the above equations and from Figure (4.19) we can notice that k for XC polymer is more effected by concentration than other polymer used in this study. And we can conclude that, in the range of polymer concentrations used in this study, k affected by concentration in the order:

$$k_{XC} > k_{CMC2} > k_{HEC} > k_{PVA} > k_{CMC1}$$









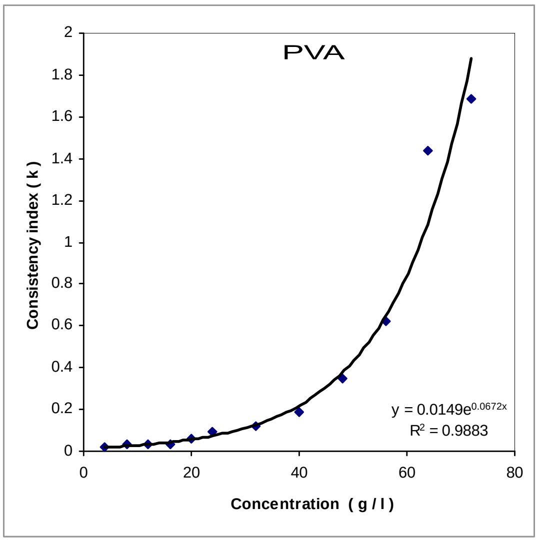


Figure (4.19)

Effect of polymer concentration on consistency index.

4.5 Effect of Polymer Type on Flow Curves

Effect of polymer type on flow curves on ordinary and logarithmic scales, at constant polymer concentrations of 4, 16 and 24 g/l, are shown in Figures (4.20), (4.21) and (4.22) respectively.

From these figures one can conclude that, at low concentrations XC polymer solutions have a higher shear stresses than other polymer solutions used in this work. At higher concentrations this phenomena is pronounced.

This is due to the molecular structure of XC polymer, which exists in disordered state in aqueous media that can be highly extended if it is subjected to shear rates.

PVA is less affected by shear rates than other polymers used.

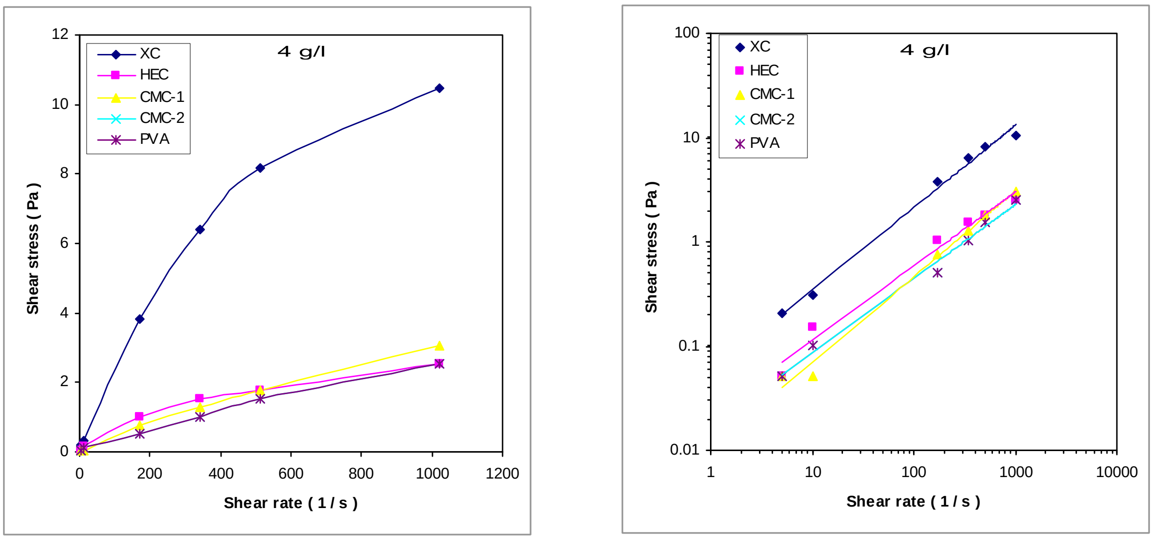


Figure (4.20) Effect of polymer type on flow curve (on ordinary and logarithmic scale), at polymer concentration of 4 g/l

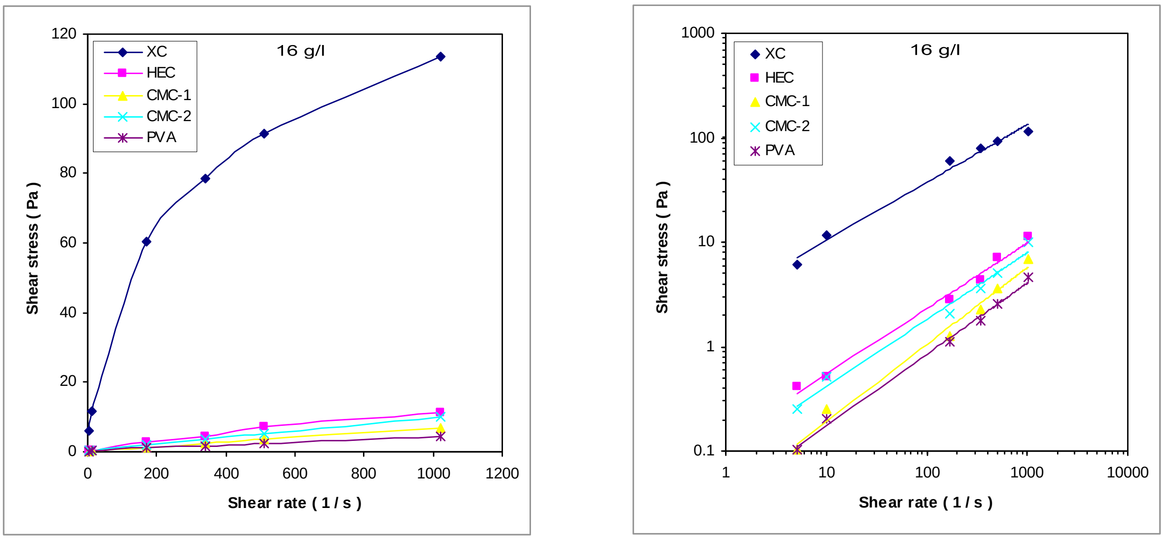


Figure (4.21) Effect of polymer type on flow curve (on ordinary and logarithmic scale), at polymer concentration of 16 g/l

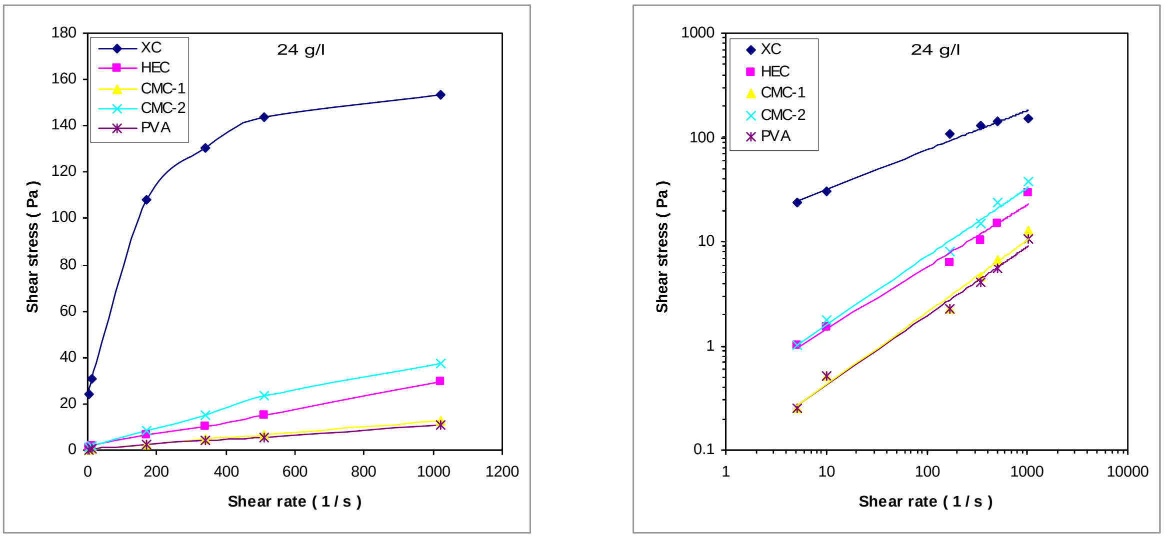


Figure (4.22) Effect of polymer type on flow curve (on ordinary and logarithmic scale), at polymer concentration of 24 g/l.

4.6 Viscosity of Polymer Solutions

The effect of concentration of each polymer used on the apparent viscosity at low concentrations are shown in Figures (4.23), (4.25), (4.27), (4.29) and (4.31), and at high polymer concentrations are shown in Figures (4.24), (4.26), (4.28), (4.30) and (4.32).

The apparent viscosity can be calculated from the power law mode, which takes the form [3]:

$$\eta_a = k\,\dot{\gamma}^{\,n-1} \qquad \ldots(4.13)$$

In general, the apparent viscosity of all polymer solutions used in this work decreases as the shear rate is increased. This behavior occurs because as the shear rate is increased the polymer molecules orient and align with the flow direction, thus reducing the drag. As the shear rate is increased further, the alignment with flow becomes more complete, and the viscosity decreases further [5].

Also from the above mentioned figures, one can notice that as the polymer concentration is increased, the decrease in viscosity was found to be more pronounced at high shear rates.

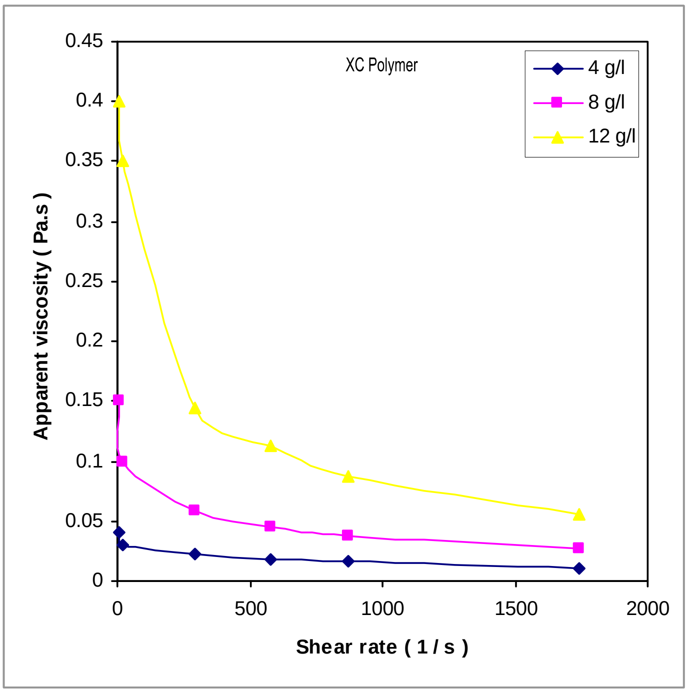


Figure (4.23) Apparent viscosity of XC polymer solutions at low concentrations

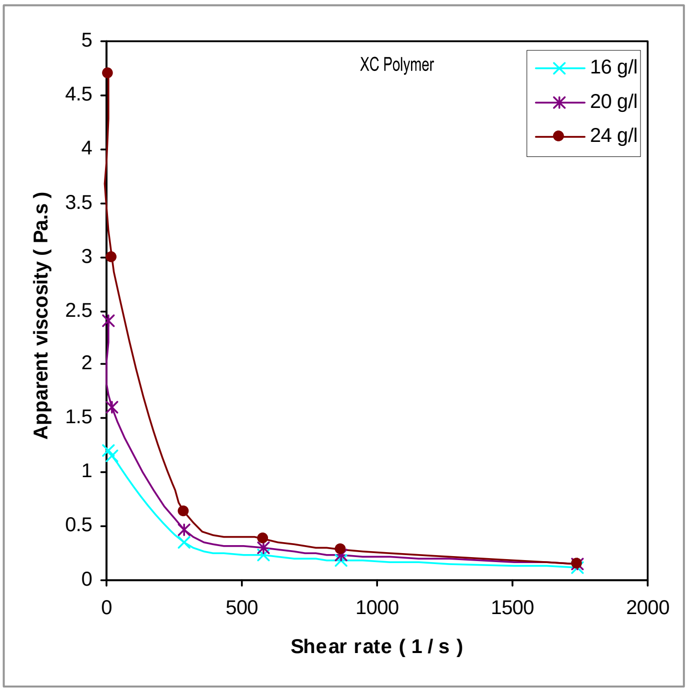


Figure (4.24) Apparent viscosity of XC polymer solutions at high concentrations

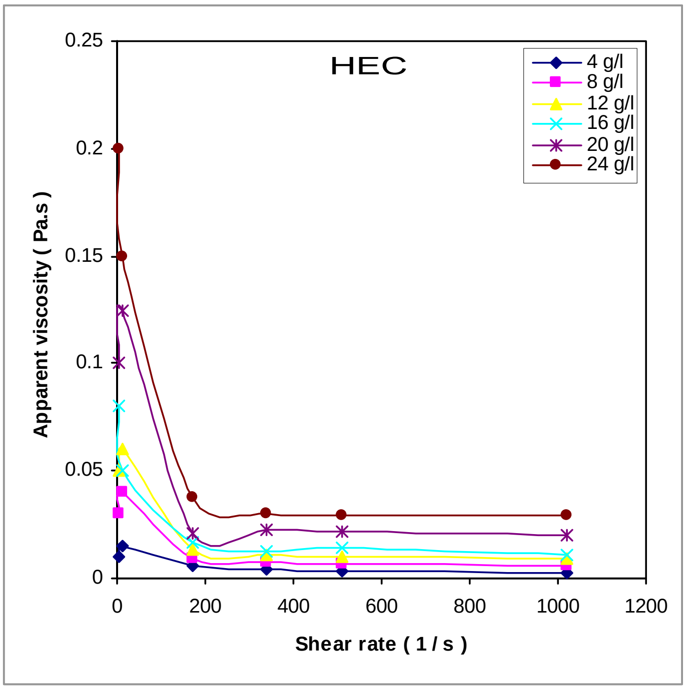


Figure (4.25) Apparent viscosity of HEC solutions at low concentrations

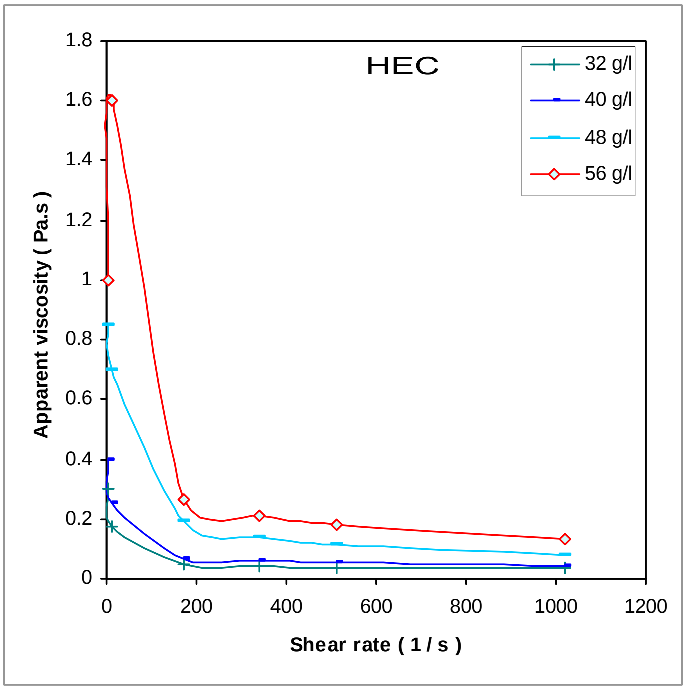


Figure (4.26) Apparent viscosity of HEC solutions at high concentrations

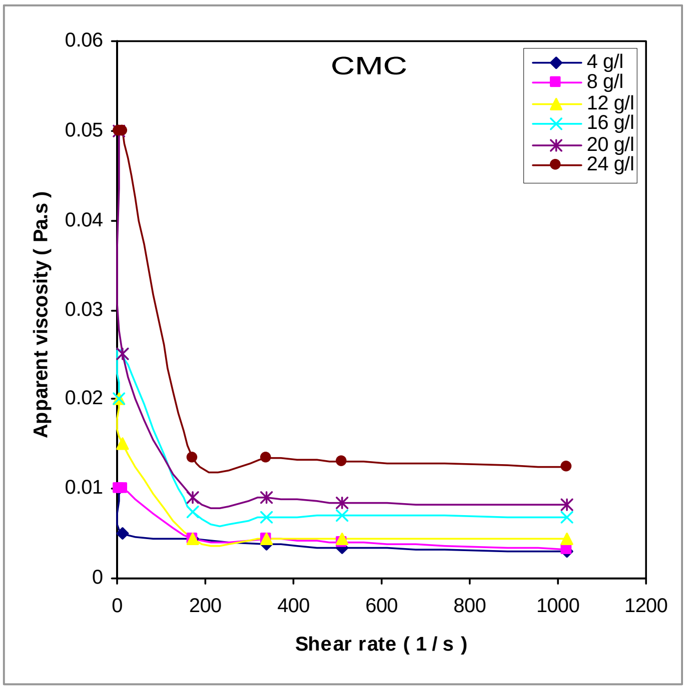


Figure (4.27) Apparent viscosity of CMC-1 solutions at low concentrations

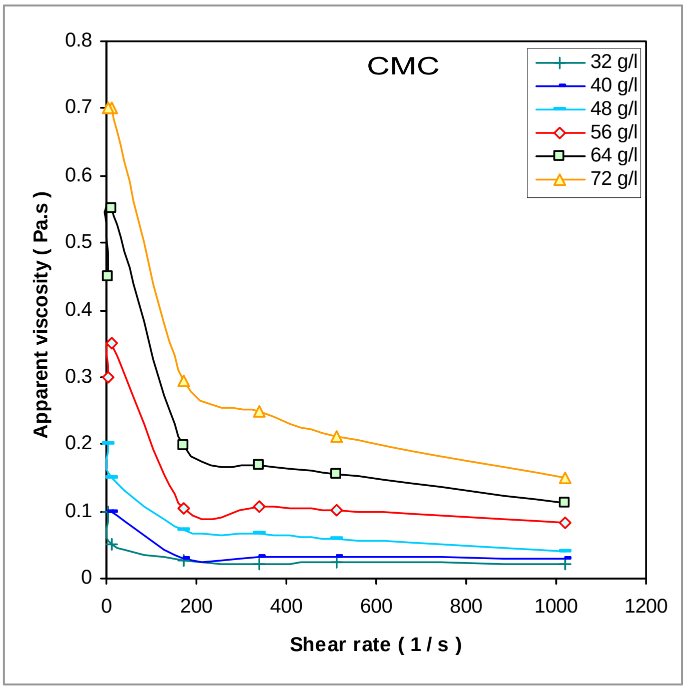


Figure (4.28) Apparent viscosity of CMC-1 solutions at low concentrations

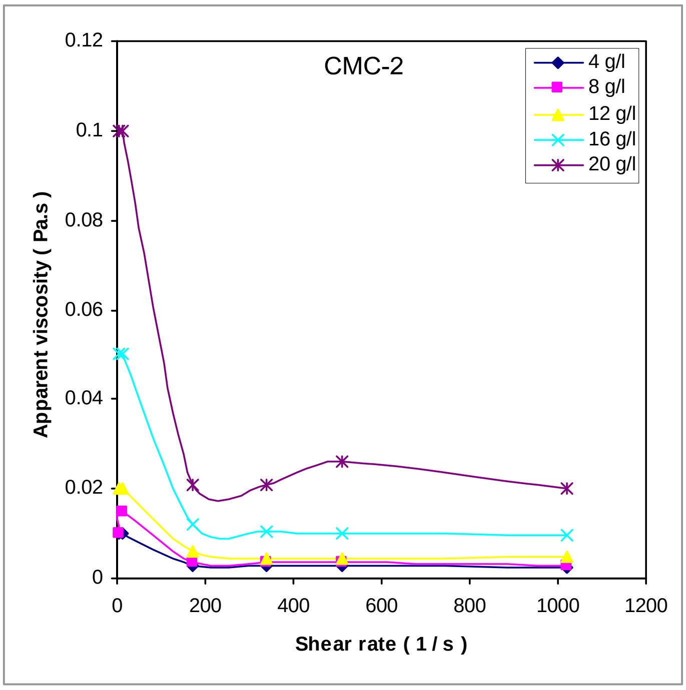


Figure (4.29) Apparent viscosity of CMC-2 solutions at low concentrations

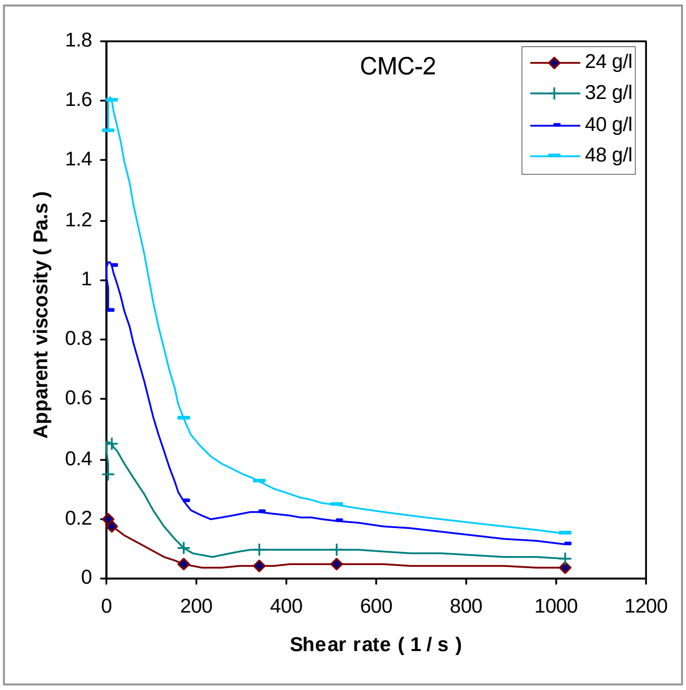


Figure (4.30) Apparent viscosity of CMC-2 solutions at high concentrations

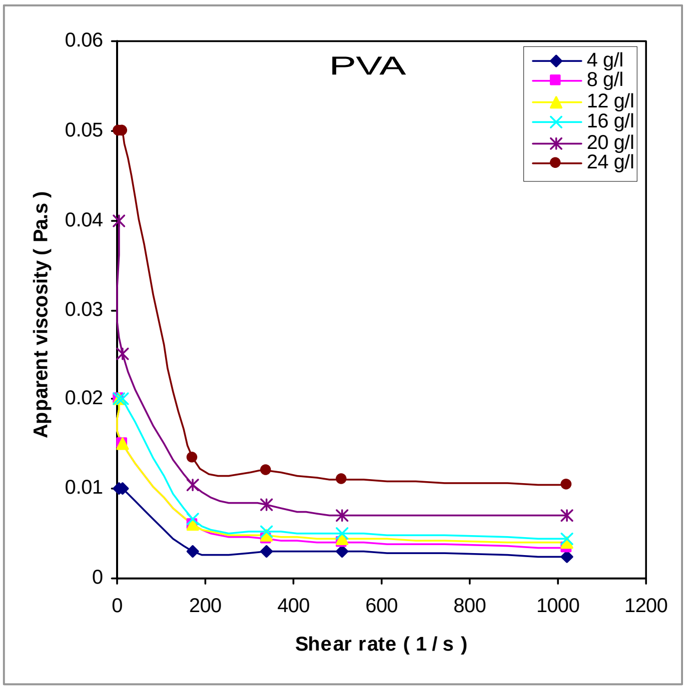


Figure (4.31) Apparent viscosity of PVA solutions at low concentrations

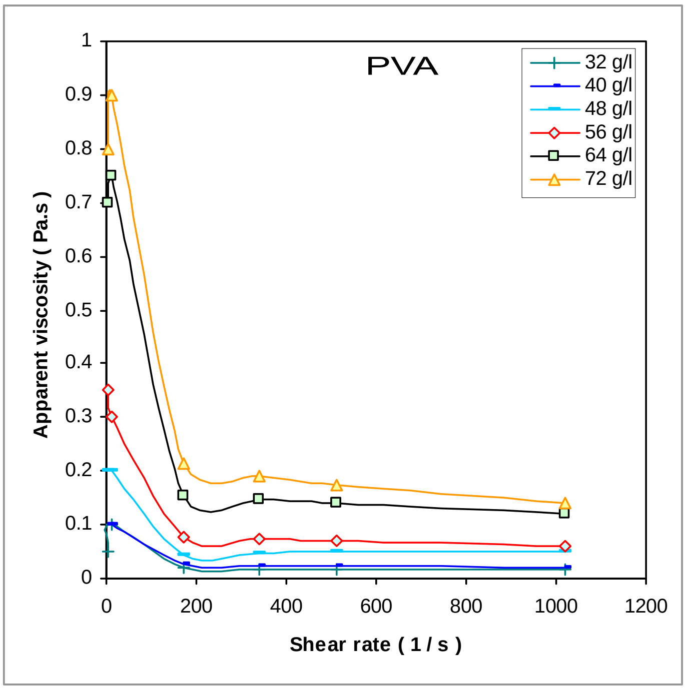


Figure (4.32) Apparent viscosity of PVA solutions at high concentrations

4.7 Effect of Polymer Type on Viscosity

The effect of polymer type on viscosity, at constant polymer concentrations of 4, 16 and 24 g/l, are shown in Figures (4.33), (4.34) and (4.35) respectively.

From these figures one can notice that XC polymer solutions have higher viscosities than other polymer solutions used in this work.

Also we can notice that a decrease in viscosity is more pronounced in XC polymer solutions than other polymers.

We can conclude that, in the range of polymer concentrations used in this study, the apparent viscosity can be ordered as:

$$\eta_{XC} > \eta_{HEC} > \eta_{CMC2} > \eta_{CMC1} > \eta_{PVA}$$

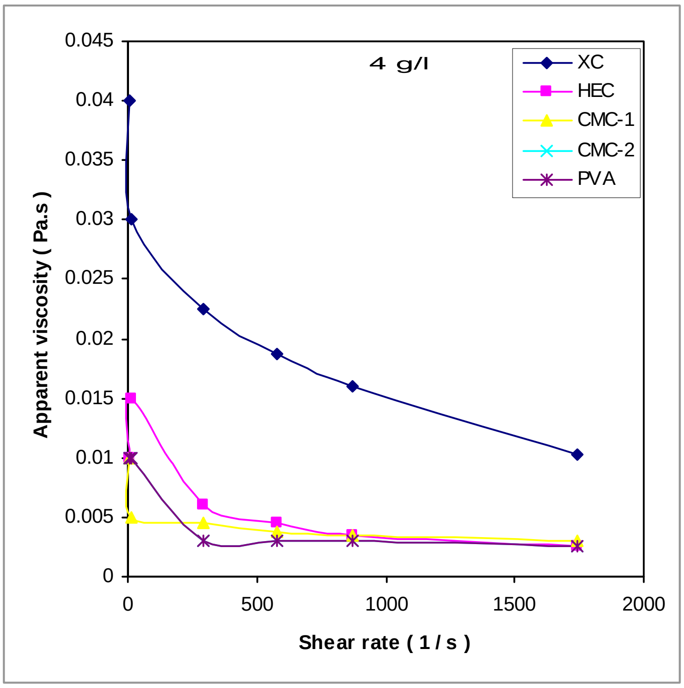


Figure (4.33) Effect of polymer type on viscosity
at polymer concentration of 4 g/l

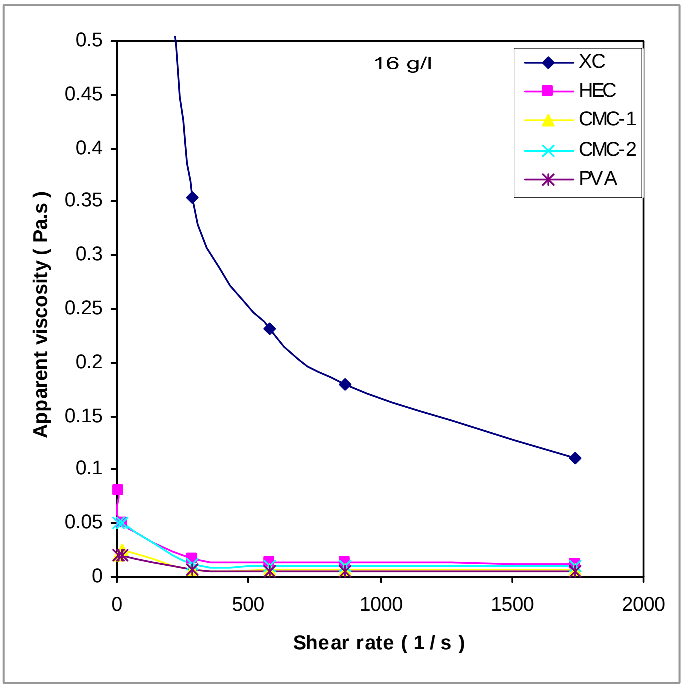


Figure (4.34) Effect of polymer type on viscosity at polymer concentration of 16 g/l

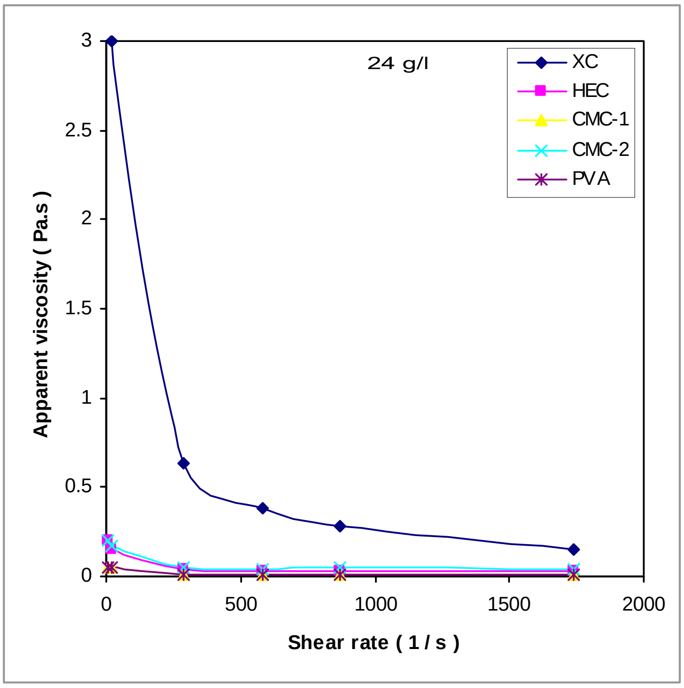


Figure (4.35) Effect of polymer type on viscosity at polymer concentration of 24 g/l

Chapter Five

Conclusions and Recommendations for Future works

5.1 Conclusions

From the present study, one can conclude the followings:

1. All polymer solutions used in this work (XC-polymer, Carboxymethyl cellulose (two types), Hydroxyethyl cellulose and Polyvinyl alcohol) behave as shear-thinning fluid, in which the viscosity decrease as the shear rate increase.

2. By using the Solver Add-in in Microsoft Excel®, the power law flow model was found to be the best fit to the experimental results.

3. As the polymer concentration is increased, the flow behavior index (n) is decreased. This behavior reflects the fact that as the polymer concentration increases the solution become far from Newtonian behavior.

4. Correlations were developed, which describe the effect of polymer concentration on the flow behavior index (n) for each polymer used in this study.

5. As the polymer concentration is increased, the consistency index (k) is increased. This behavior reflects the fact that as the polymer concentration increases the solution become thicker.

6. Correlations were developed, which describe the effect of polymer concentration on the consistency index (k) for each polymer used in this study.

7. XC-polymer solutions have a higher viscosity, and its viscosity decreases much more than other polymer solutions used in this study.

5.2 Recommendations for Future Works

1. Studying the effect of temperature on the rheological properties of polymer solutions.

2. Studying the rheological properties at different (lower or higher) shear rates used in this work, this may have useful industrial applications.

3. Using other methods (rather than standard rheometric techniques), such as particle tracking method to study the rheological properties of polymer solutions.

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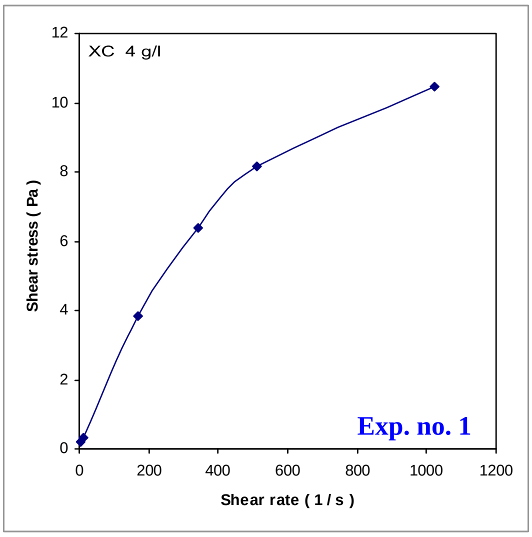
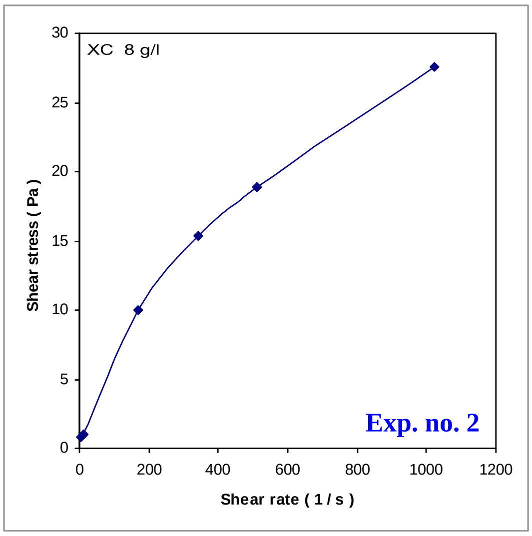
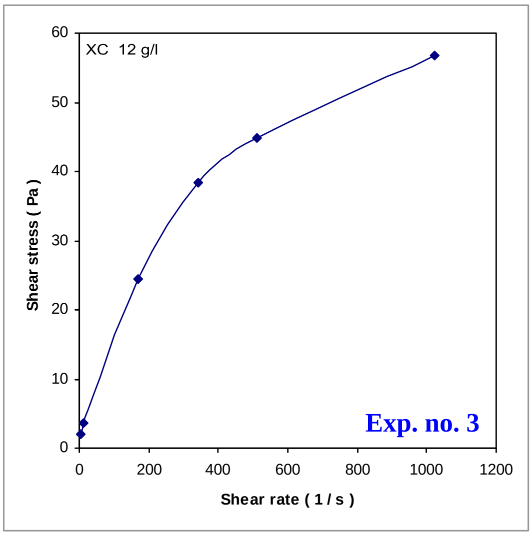
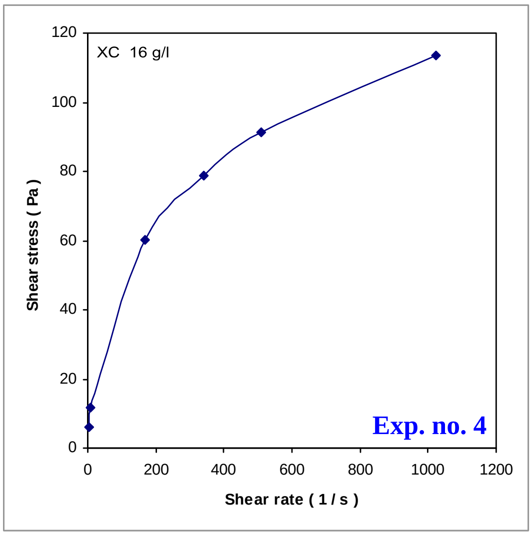
Appendix A

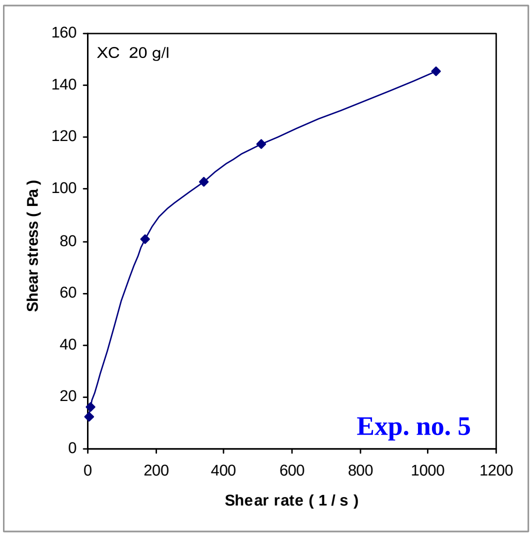
The Flow Curves of the Experiments

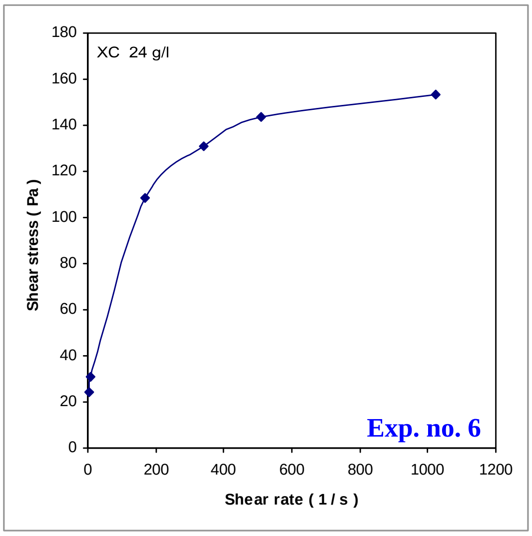


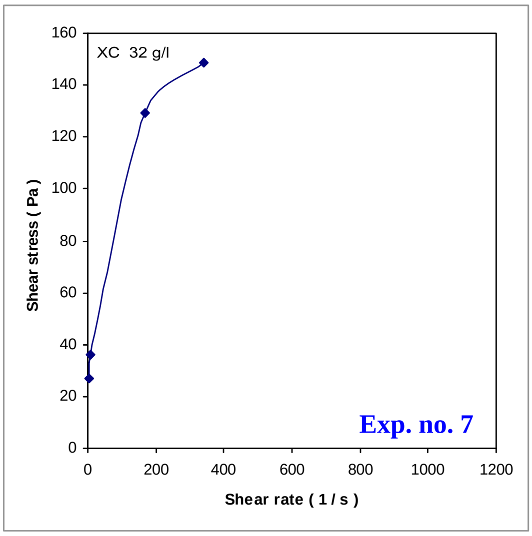








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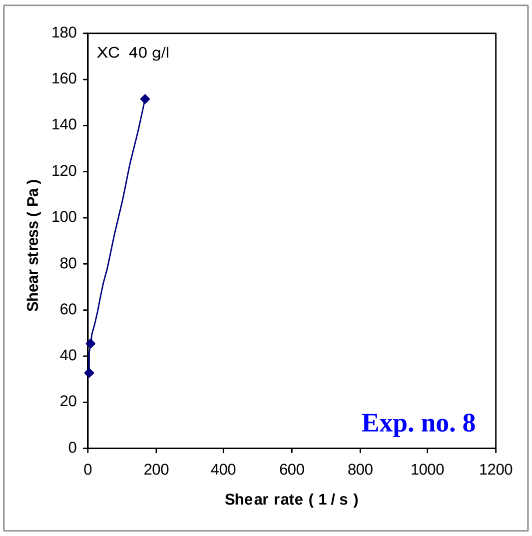
1000
1200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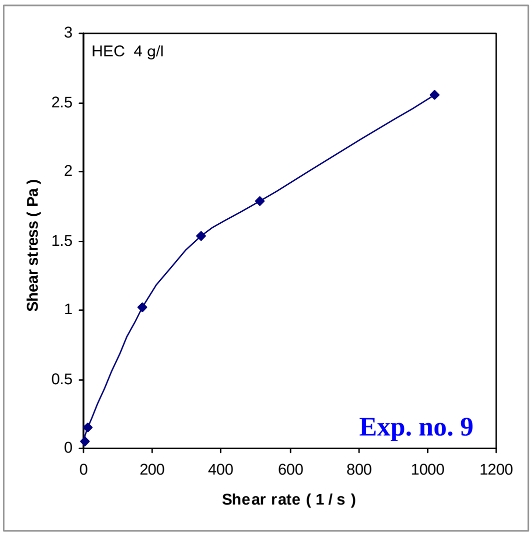
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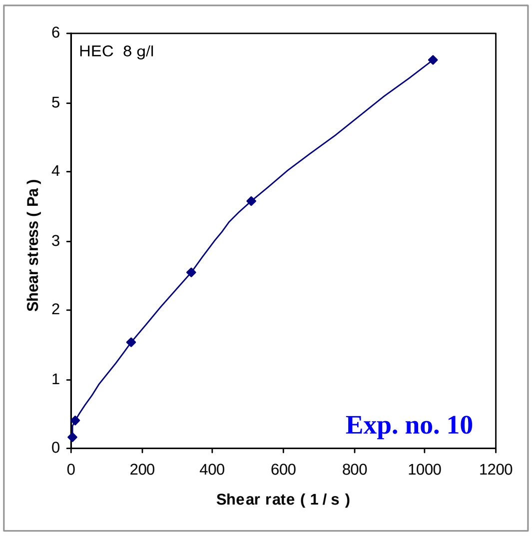
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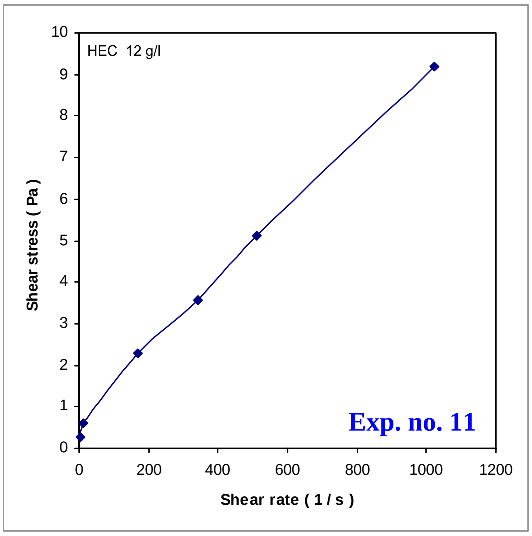
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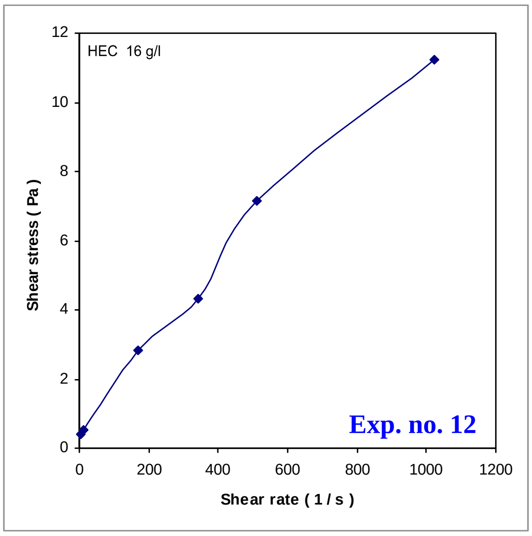
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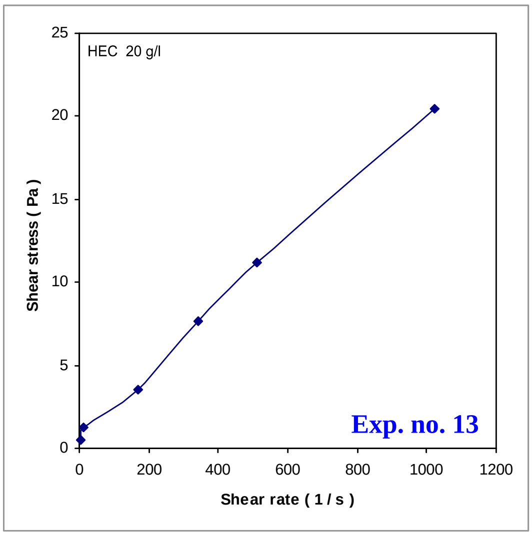
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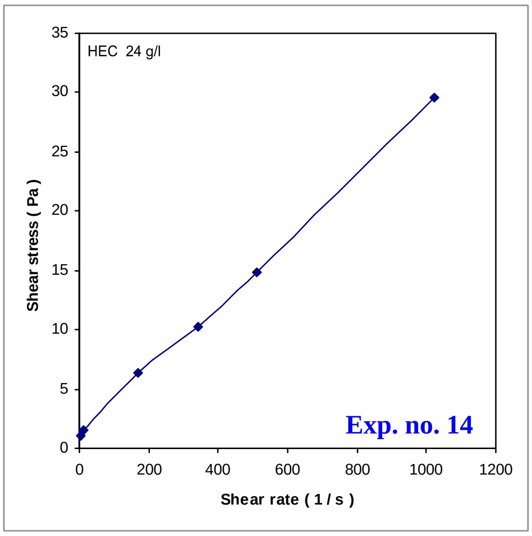
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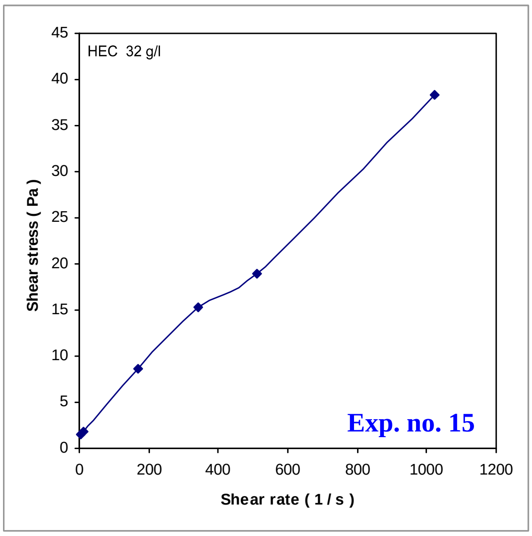
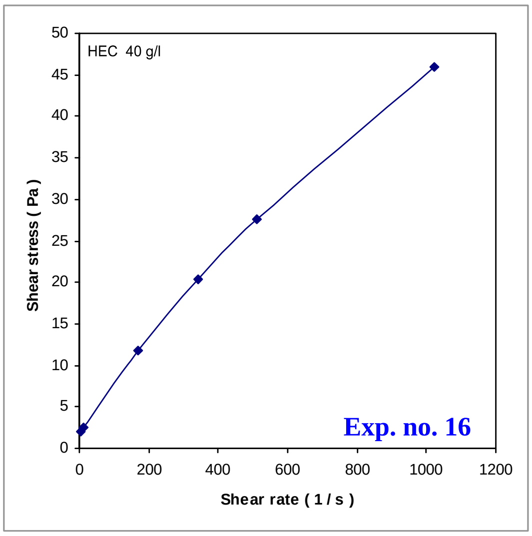
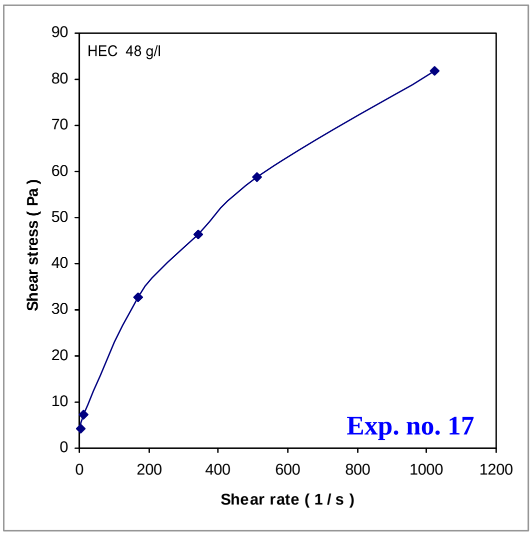
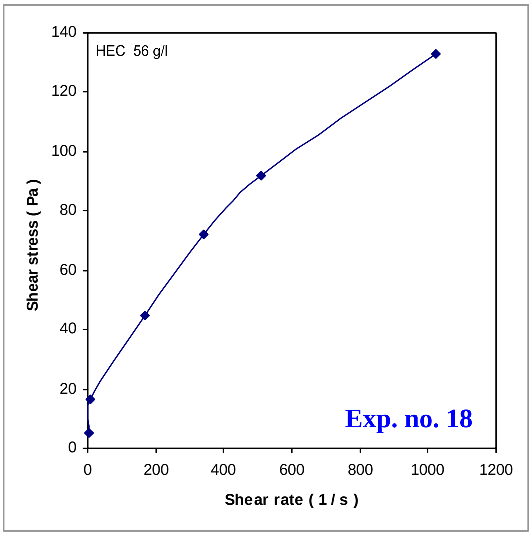
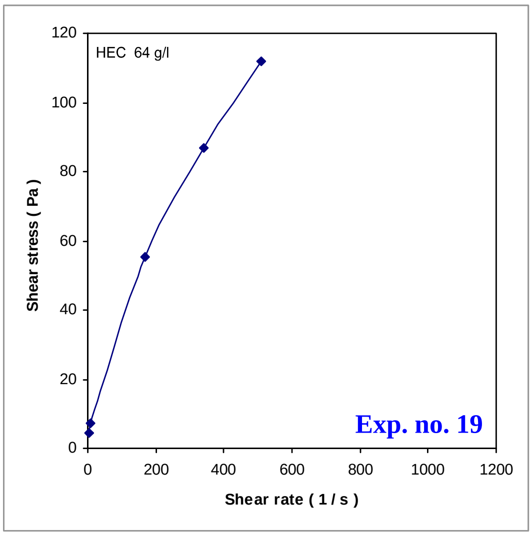
1000
1200

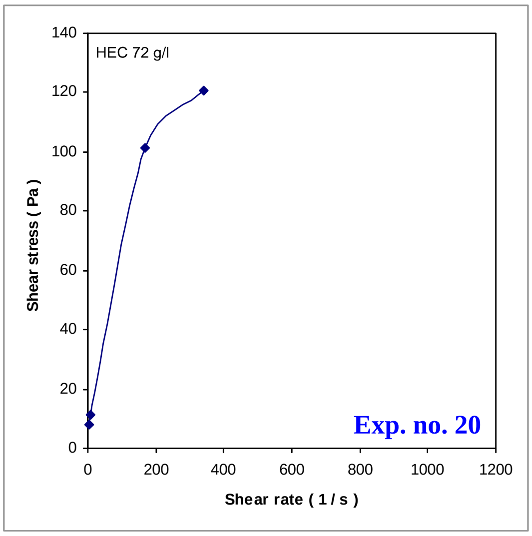

HEC 32 g/l
Exp. no. 15
Shear stress (Pa)
0
5
10
15
20
25
30
35
40
45
Shear rate (1 / s)
0
200
400
600
800
1000
1200

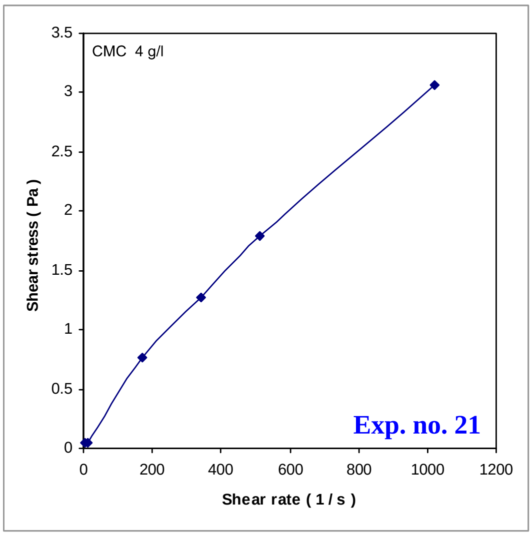

HEC 40 g/l
Exp. no. 16
Shear stress (Pa)
0
5
10
15
20
25
30
35
40
45
50
Shear rate (1 / s)
0
200
400
600
800
1000
1200

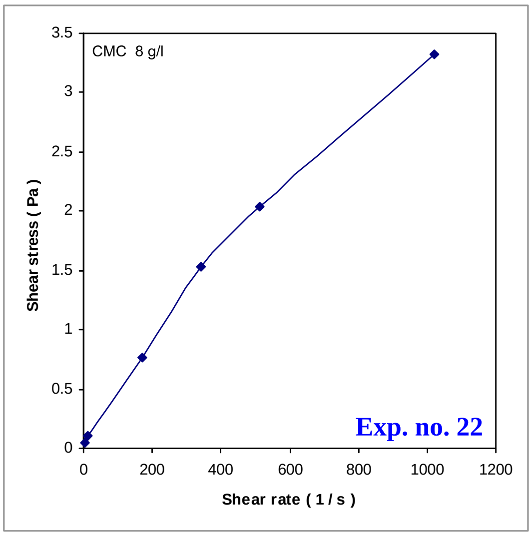

HEC 48 g/l
Exp. no. 17
Shear stress (Pa)
0
10
20
30
40
50
60
70
80
90
Shear rate (1 / s)
0
200
400
600
800
1000
1200

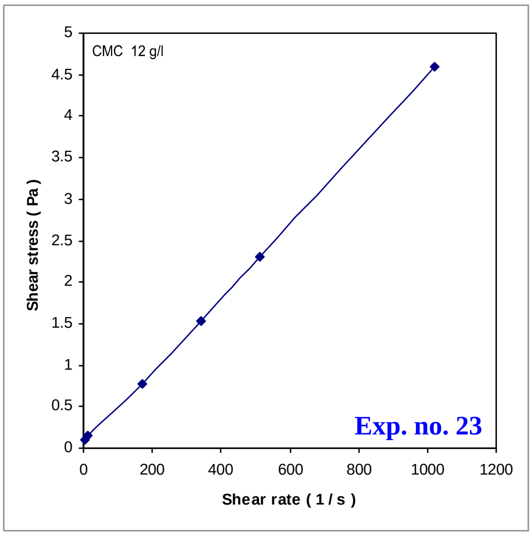

HEC 56 g/l
Exp. no. 18
Shear stress (Pa)
0
20
40
60
80
100
120
140
Shear rate (1 / s)
0
200
400
600
800
1000
1200

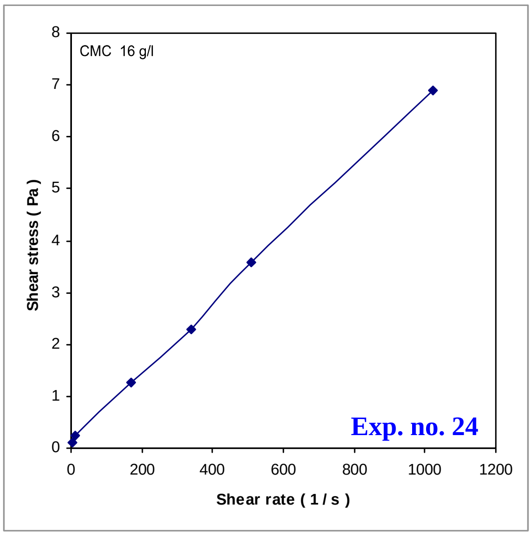

HEC 64 g/l
Shear stress (Pa)
120
100
80
60
40
20
0
0
200
400
600
800
1000
1200
Shear rate (1 / s)
Exp. no. 19

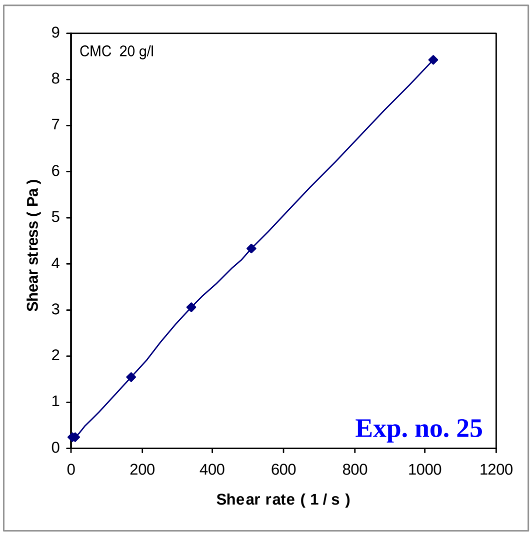

HEC 72 g/l
Shear stress (Pa)
140
120
100
80
60
40
20
0
0
200
400
600
800
1000
1200
Shear rate (1 / s)
Exp. no. 20

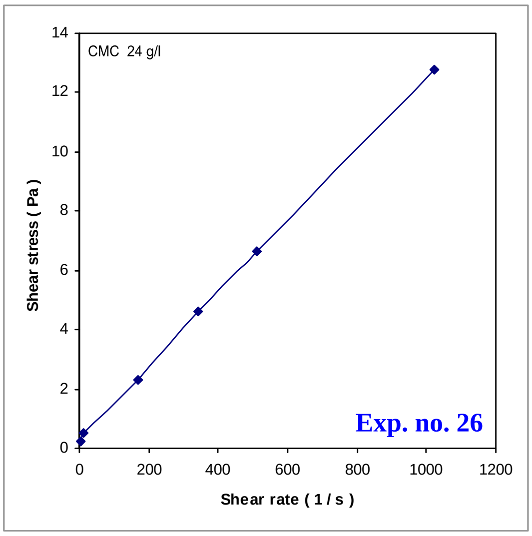

CMC 4 g/l
Shear stress (Pa)
3.5
3
2.5
2
1.5
1
0.5
0
0
200
400
600
800
1000
1200
Shear rate (1 / s)
Exp. no. 21

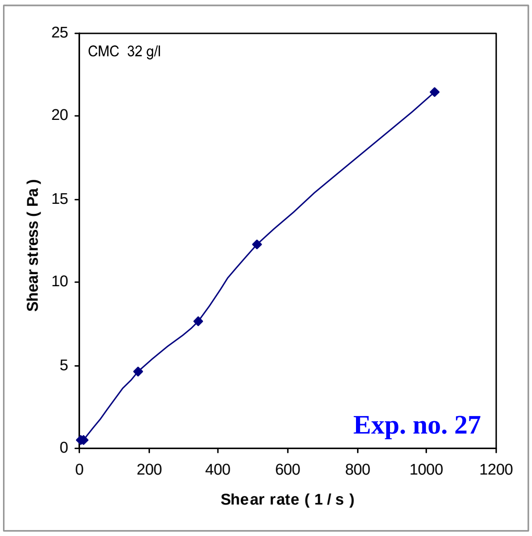

CMC 8 g/l
Shear stress (Pa)
3.5
3
2.5
2
1.5
1
0.5
0
0
200
400
600
800
1000
1200
Shear rate (1 / s)
Exp. no. 22

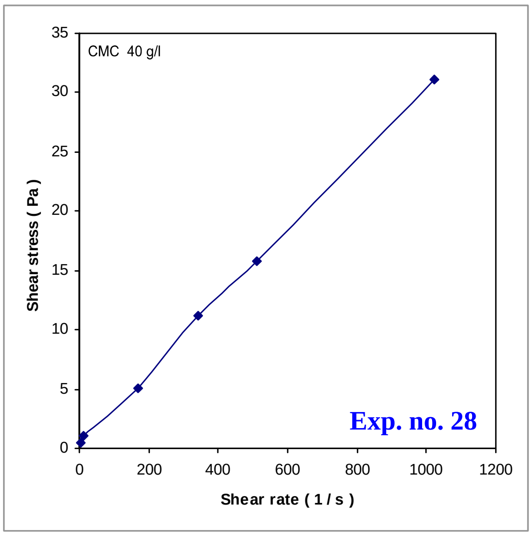

CMC 12 g/l
Shear stress (Pa)
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
200
400
600
800
1000
1200
Shear rate (1 / s)
Exp. no. 23

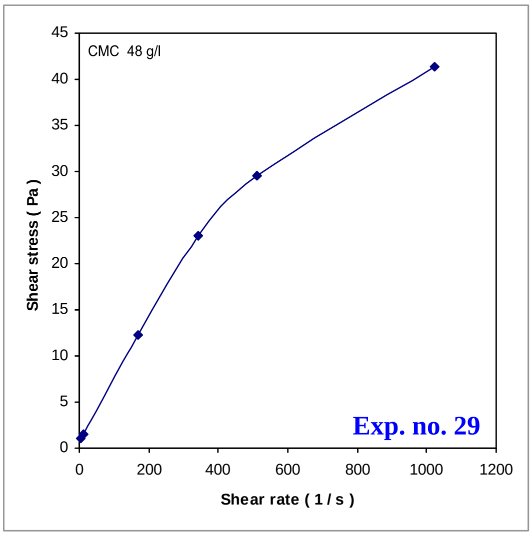

CMC 16 g/l
Shear stress (Pa)
8
7
6
5
4
3
2
1
0
0
200
400
600
800
1000
1200
Shear rate (1 / s)
Exp. no. 24

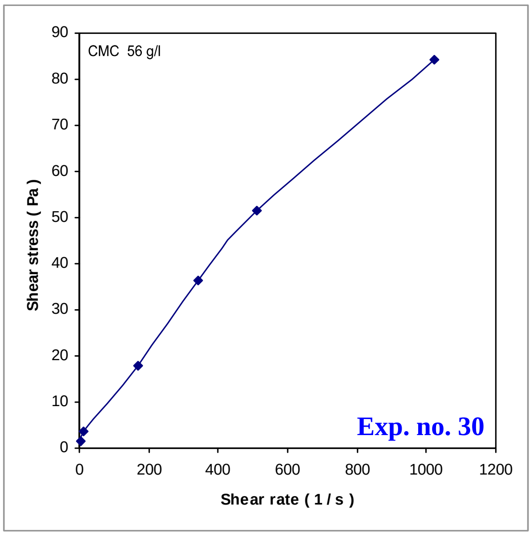

CMC 20 g/l
Shear stress (Pa)
Shear rate (1 / s)
0
1
2
3
4
5
6
7
8
9
0
200
400
600
800
1000
1200
Exp. no. 25

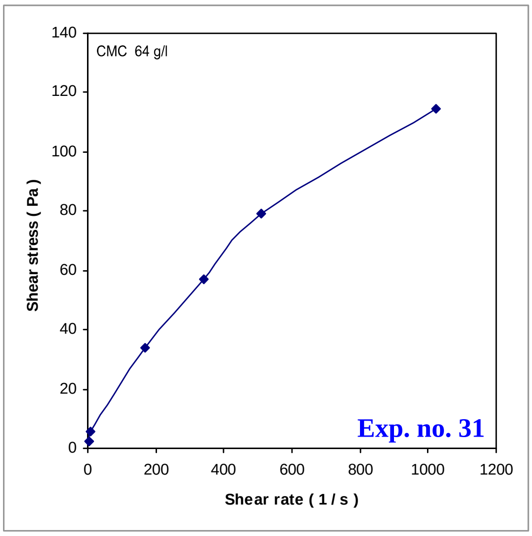

CMC 24 g/l
Shear stress (Pa)
Shear rate (1 / s)
0
2
4
6
8
10
12
14
0
200
400
600
800
1000
1200
Exp. no. 26

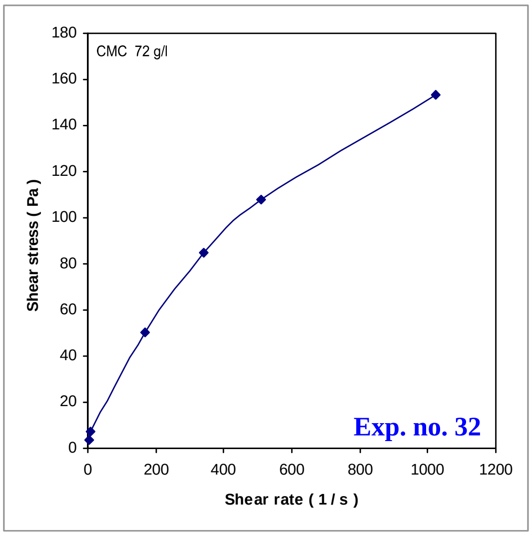

CMC 32 g/l
Shear stress (Pa)
Shear rate (1 / s)
0
5
10
15
20
25
0
200
400
600
800
1000
1200
Exp. no. 27

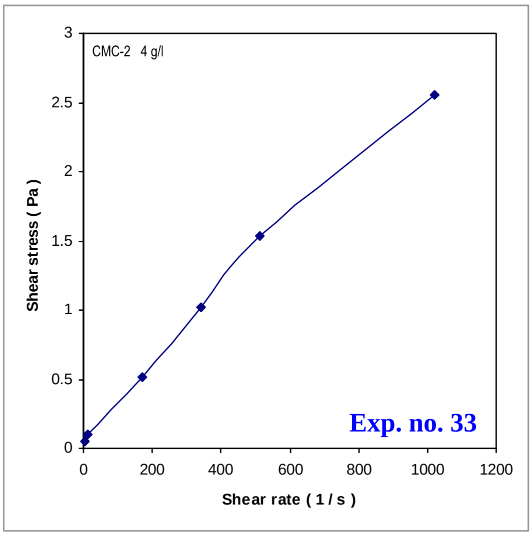

CMC 40 g/l
Shear stress (Pa)
Shear rate (1 / s)
0
5
10
15
20
25
30
35
0
200
400
600
800
1000
1200
Exp. no. 28

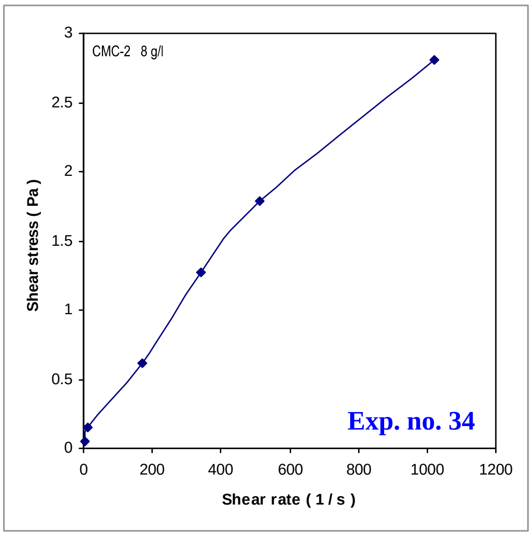

CMC 48 g/l
Shear stress (Pa)
Shear rate (1 / s)
0
5
10
15
20
25
30
35
40
45
0
200
400
600
800
1000
1200
Exp. no. 29

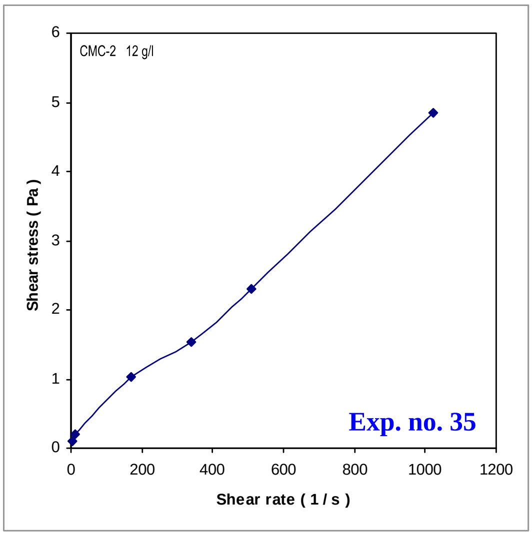

CMC 56 g/l
Shear stress (Pa)
Shear rate (1 / s)
0
10
20
30
40
50
60
70
80
90
0
200
400
600
800
1000
1200
Exp. no. 30

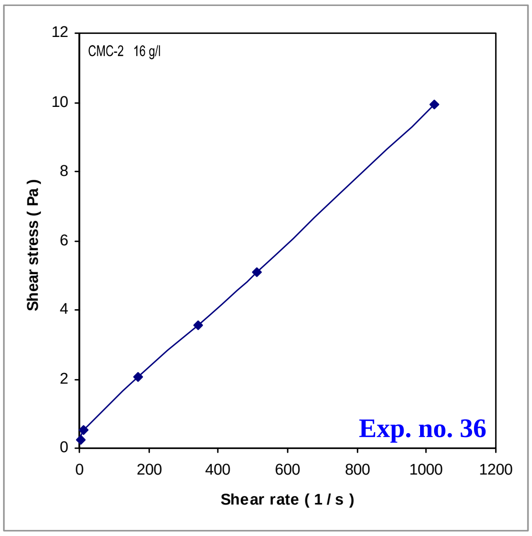

CMC 64 g/l
Exp. no. 31
Shear stress (Pa)
0
20
40
60
80
100
120
140
Shear rate (1 / s)
0
200
400
600
800
1000
1200

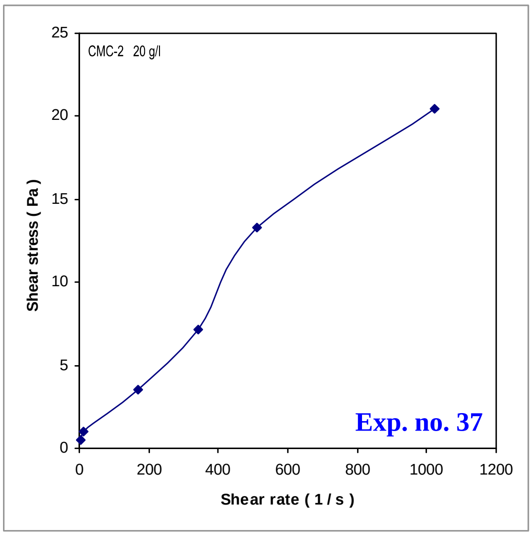

CMC 72 g/l
Exp. no. 32
Shear stress (Pa)
0
20
40
60
80
100
120
140
160
180
Shear rate (1 / s)
0
200
400
600
800
1000
1200

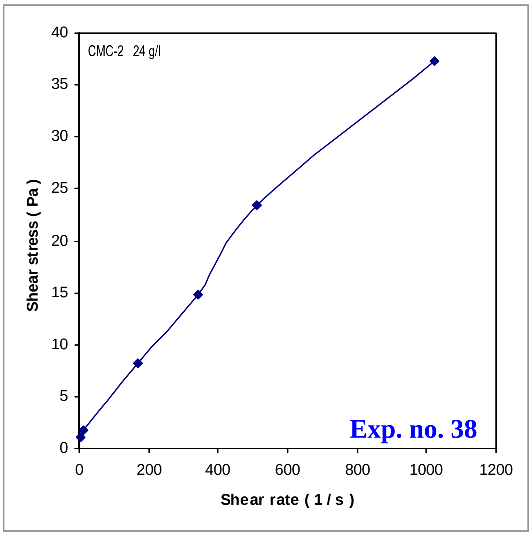

CMC-2 4 g/l
Exp. no. 33
Shear stress (Pa)
0
0.5
1
1.5
2
2.5
3
Shear rate (1 / s)
0
200
400
600
800
1000
1200

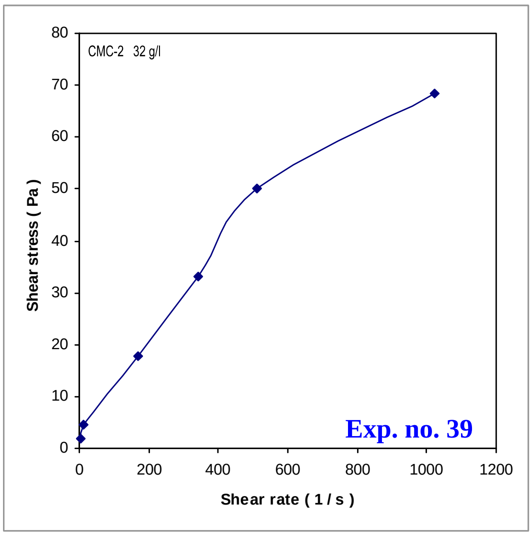

CMC-2 8 g/l
Exp. no. 34
Shear stress (Pa)
0
0.5
1
1.5
2
2.5
3
Shear rate (1 / s)
0
200
400
600
800
1000
1200

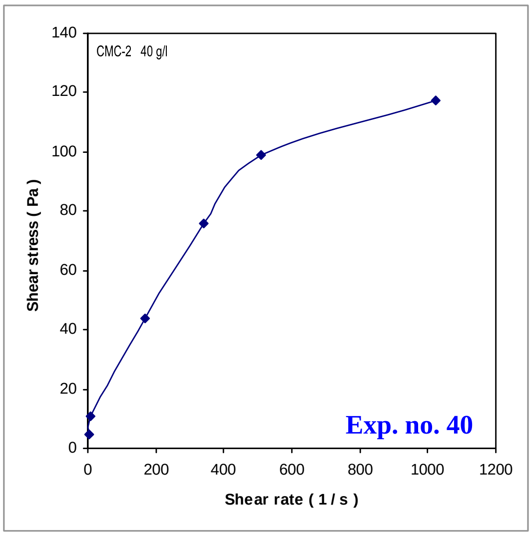

CMC-2 12 g/l
Exp. no. 35
Shear stress (Pa)
0
1
2
3
4
5
6
Shear rate (1 / s)
0
200
400
600
800
1000
1200

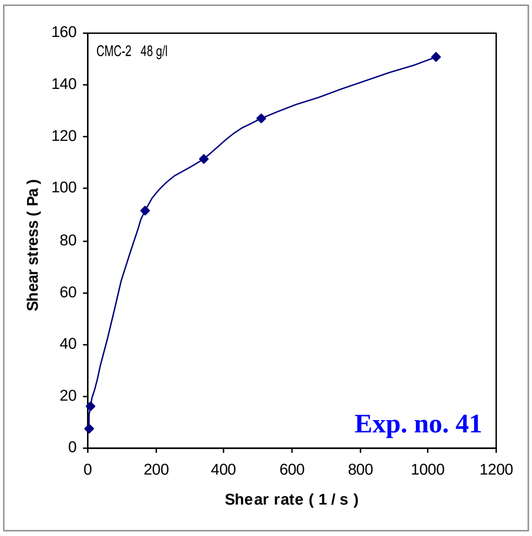

CMC-2 16 g/l
Exp. no. 36
Shear stress (Pa)
0
2
4
6
8
10
12
Shear rate (1 / s)
0
200
400
600
800
1000
1200

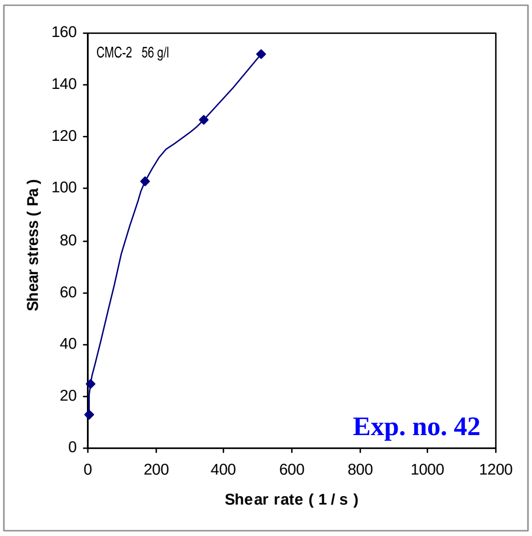

CMC-2 20 g/l
Shear stress (Pa)
0
5
10
15
20
25
0
200
400
600
800
1000
1200
Shear rate (1 / s)
Exp. no. 37

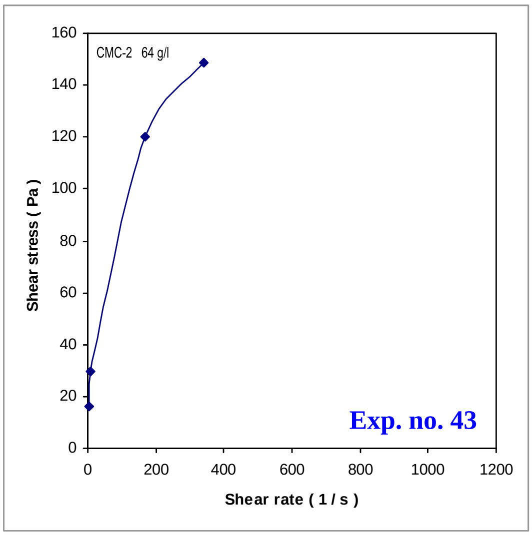

CMC-2 24 g/l
Shear stress (Pa)
0
5
10
15
20
25
30
35
40
0
200
400
600
800
1000
1200
Shear rate (1 / s)
Exp. no. 38

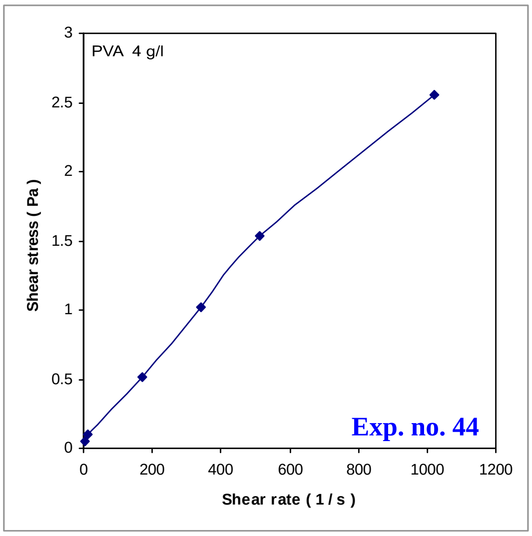

CMC-2 32 g/l
Shear stress (Pa)
0
10
20
30
40
50
60
70
80
0
200
400
600
800
1000
1200
Shear rate (1 / s)
Exp. no. 39

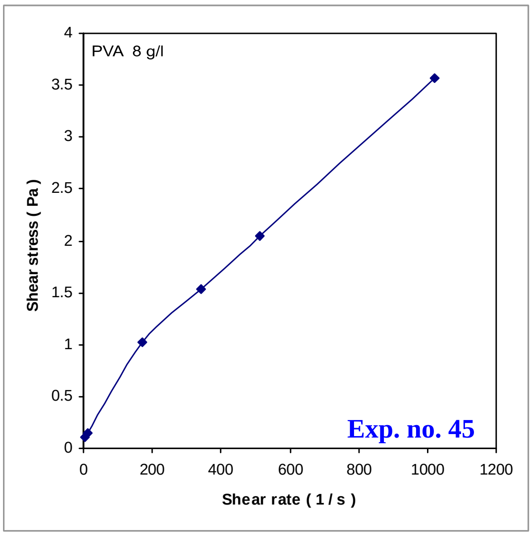

CMC-2 40 g/l
Shear stress (Pa)
0
20
40
60
80
100
120
140
0
200
400
600
800
1000
1200
Shear rate (1 / s)
Exp. no. 40

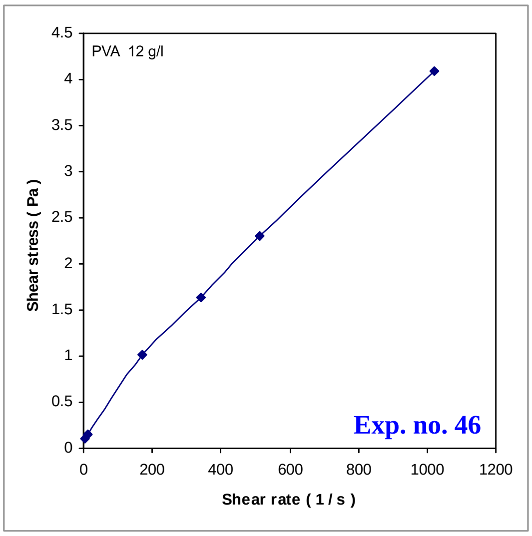

CMC-2 48 g/l
Shear stress (Pa)
0
20
40
60
80
100
120
140
160
0
200
400
600
800
1000
1200
Shear rate (1 / s)
Exp. no. 41

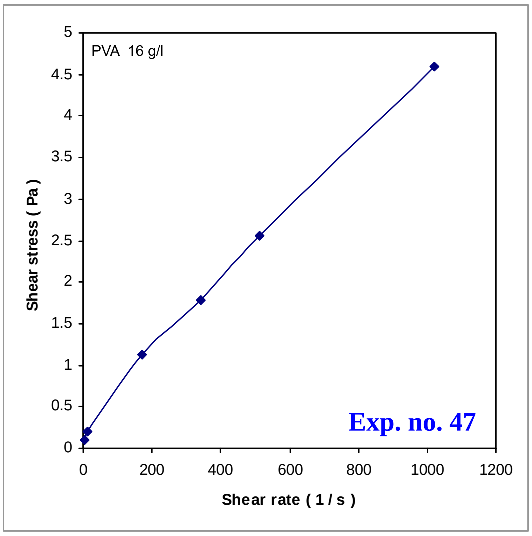

CMC-2 56 g/l
Shear stress (Pa)
0
20
40
60
80
100
120
140
160
0
200
400
600
800
1000
1200
Shear rate (1 / s)
Exp. no. 42

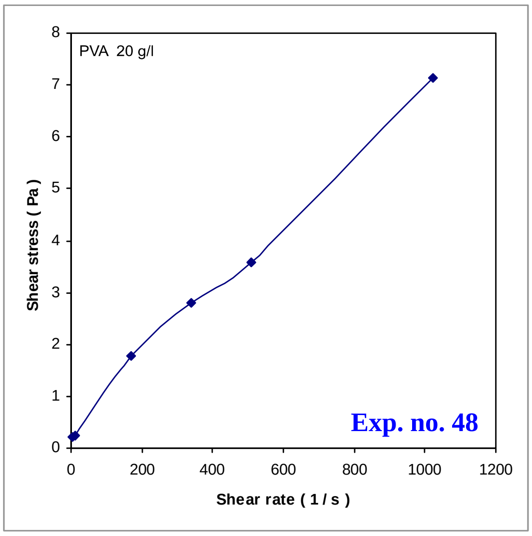

CMC-2 64 g/l
Exp. no. 43
Shear stress (Pa)
Shear rate (1 / s)
0
20
40
60
80
100
120
140
160
0
200
400
600
800
1000
1200

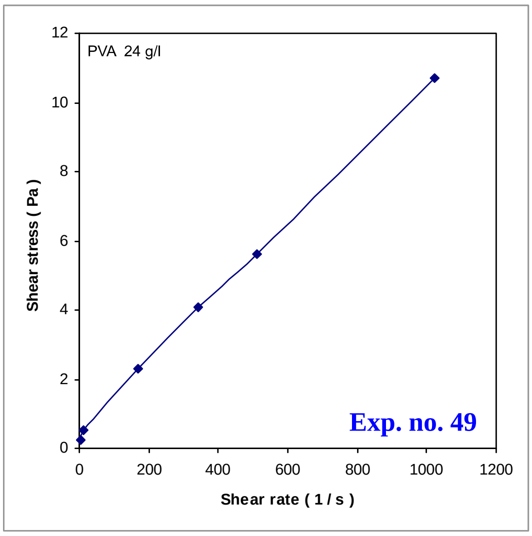

PVA 4 g/l
Exp. no. 44
Shear stress (Pa)
Shear rate (1 / s)
0
0.5
1
1.5
2
2.5
3
0
200
400
600
800
1000
1200

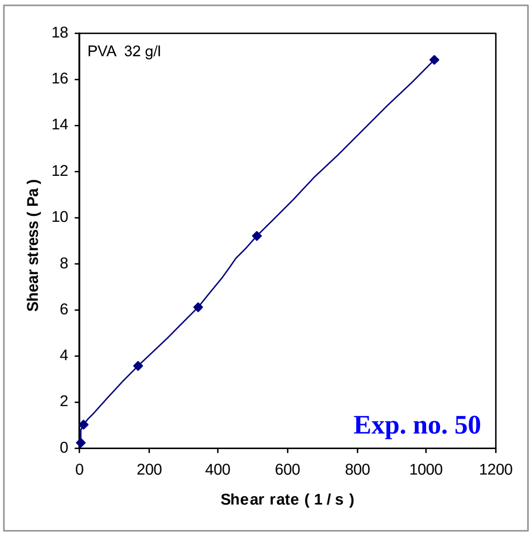

PVA 8 g/l
Exp. no. 45
Shear stress (Pa)
Shear rate (1 / s)
0
0.5
1
1.5
2
2.5
3
3.5
4
0
200
400
600
800
1000
1200

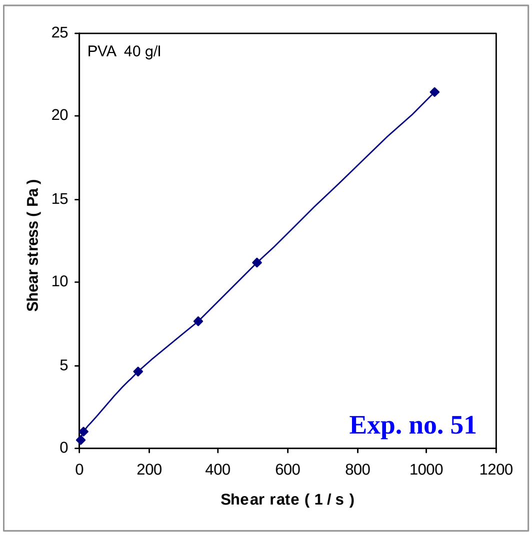

PVA 12 g/l
Exp. no. 46
Shear stress (Pa)
Shear rate (1 / s)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
0
200
400
600
800
1000
1200

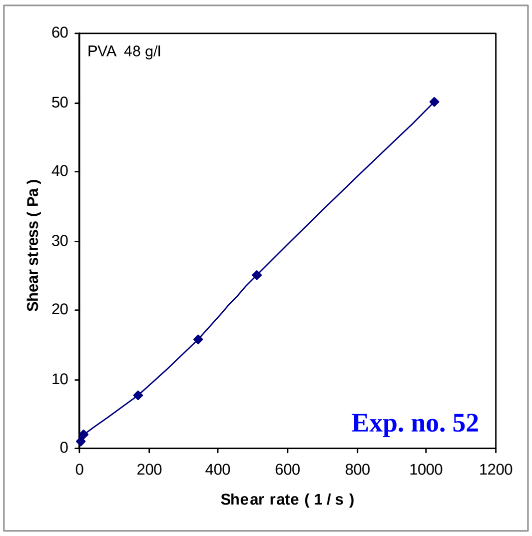

PVA 16 g/l
Exp. no. 47
Shear stress (Pa)
Shear rate (1 / s)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
0
200
400
600
800
1000
1200

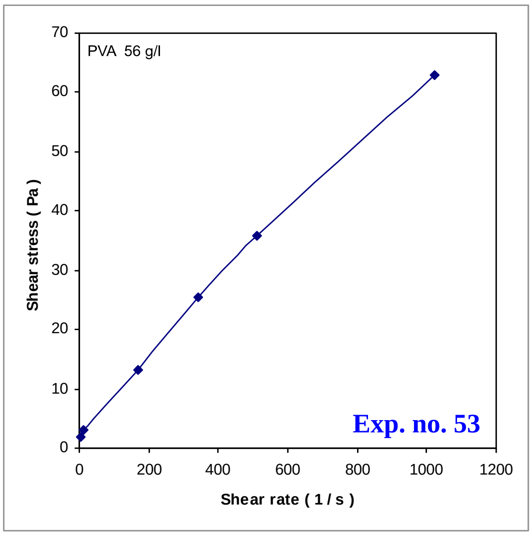

PVA 20 g/l
Exp. no. 48
Shear stress (Pa)
Shear rate (1 / s)
0
1
2
3
4
5
6
7
8
0
200
400
600
800
1000
1200

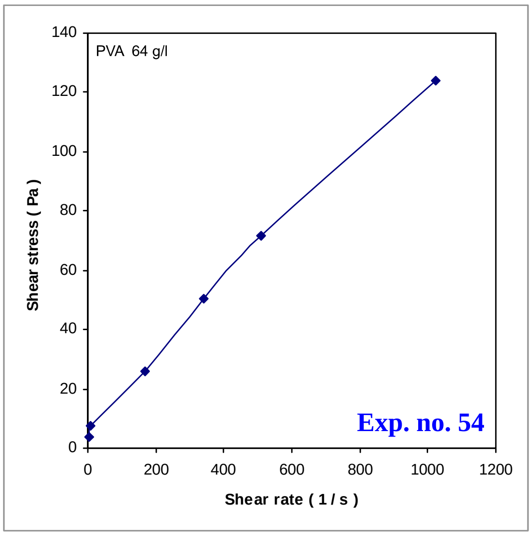

PVA 24 g/l
Exp. no. 49
Shear stress (Pa)
Shear rate (1 / s)
0
2
4
6
8
10
12
0
200
400
600
800
1000
1200

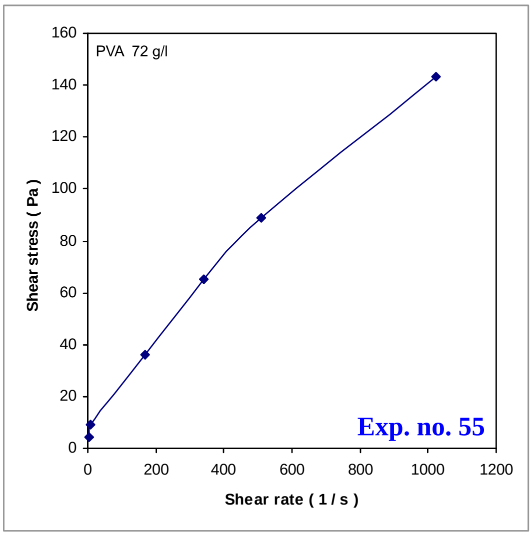

PVA 32 g/l
Exp. no. 50
Shear stress (Pa)
Shear rate (1 / s)
0
2
4
6
8
10
12
14
16
18
0
200
400
600
800
1000
1200


PVA 40 g/l
Exp. no. 51
Shear stress (Pa)
Shear rate (1 / s)
0
5
10
15
20
25
0
200
400
600
800
1000
1200


PVA 48 g/l
Exp. no. 52
Shear stress (Pa)
Shear rate (1 / s)
0
10
20
30
40
50
60
0
200
400
600
800
1000
1200


PVA 56 g/l
Exp. no. 53
Shear stress (Pa)
Shear rate (1 / s)
0
10
20
30
40
50
60
70
0
200
400
600
800
1000
1200


PVA 64 g/l
Exp. no. 54
Shear stress (Pa)
Shear rate (1 / s)
0
20
40
60
80
100
120
140
0
200
400
600
800
1000
1200


PVA 72 g/l
Exp. no. 55
Shear stress (Pa)
0
20
40
60
80
100
120
140
160
Shear rate (1 / s)
0
200
400
600
800
1000
1200

Appendix B

Flow Model Selection Using Add-in in Microsoft Excel

Table(B.1) Model selection for HEC solutions using Add-in in Microsoft Excel.

Exp. No.	**Conc. (g /l)**	**Sum of Square Error**					
		Newtonian Eqn.(2.4)	**Bingham Eqn.(2.8)**	**Power Law Eqn.(2.9)**	**With Yield Eqn.(2.10)**	**Casson Eqn.(2.11)**	**Robertson Eqn.(2.12)**
9	4	1.376	0.616	0.243	0.243	0.731	0.243
10	8	1.386	0.342	0.144	0.144	0.226	0.144
11	12	1.371	0.256	0.138	0.138	0.165	0.138
12	16	1.306	0.048	0.017	0.016	0.017	0.017
13	20	1.293	0.246	0.245	0.243	0.229	0.245
14	24	1.368	0.051	0.038	0.038	0.028	0.038
15	32	1.374	0.027	0.018	0.011	0.013	0.018
16	40	1.436	0.048	0.003	0.002	0.004	0.003
17	48	1.823	0.316	0.010	0.010	0.150	0.010
18	56	1.731	0.551	0.235	0.235	0.389	0.235

Table(B.2) Model selection for CMC-1 solutions using Add-in in Microsoft Excel.

Exp. No.	**Conc. (g /l)**	**Sum of Square Error**					
		Newtonian Eqn.(2.4)	**Bingham Eqn.(2.8)**	**Power Law Eqn.(2.9)**	**With Yield Eqn.(2.10)**	**Casson Eqn.(2.11)**	**Robertson Eqn.(2.12)**
21	4	0.543	0.128	0.166	0.148	0.702	0.166
22	8	0.763	0.138	0.025	0.025	0.462	0.025
23	12	1.055	0.031	0.030	0.030	0.044	0.030
24	16	0.907	0.189	0.155	0.150	0.140	0.155
25	20	1.083	0.015	0.028	0.014	0.062	0.028
26	24	1.057	0.114	0.102	0.102	0.084	0.102
27	32	0.866	0.044	0.043	0.043	0.069	0.043
28	40	0.912	0.108	0.104	0.104	0.089	0.104
29	48	1.122	0.197	0.031	0.031	0.111	0.031
30	56	0.988	0.195	0.109	0.108	0.127	0.109
31	64	1.142	0.332	0.082	0.082	0.215	0.082
32	72	1.237	0.316	0.042	0.042	0.190	0.042

Table(B.3) Model selection for CMC-2 solutions using Add-in in Microsoft Excel.

Exp. No.	Conc. (g /l)	Sum of Square Error					
		Newtonian Eqn.(2.4)	**Bingham Eqn.(2.8)**	**Power Law Eqn.(2.9)**	**With Yield Eqn.(2.10)**	**Casson Eqn.(2.11)**	**Robertson Eqn.(2.12)**
33	4	1.013	0.123	0.107	0.108	0.076	0.107
34	8	1.085	0.332	0.210	0.210	0.252	0.210
35	12	1.170	0.150	0.109	0.109	0.096	0.109
36	16	1.250	0.135	0.105	0.105	0.087	0.105
37	20	1.239	0.174	0.173	0.173	0.171	0.173
38	24	1.209	0.100	0.060	0.060	0.052	0.060
39	32	1.337	0.340	0.154	0.154	0.229	0.154
40	40	1.776	0.528	0.127	0.127	0.339	0.127
41	48	2.181	0.754	0.202	0.202	0.520	0.202

Table(B.4) Model selection for PVA solutions using Add-in in Microsoft Excel.

Exp. No.	Conc. (g /l)	Sum of Square Error					
		Newtonian Eqn.(2.4)	**Bingham Eqn.(2.8)**	**Power Law Eqn.(2.9)**	**With Yield Eqn.(2.10)**	**Casson Eqn.(2.11)**	**Robertson Eqn.(2.12)**
44	4	1.013	0.123	0.107	0.085	0.077	0.107
45	8	1.249	0.120	0.006	0.006	0.042	0.006
46	12	1.110	0.072	0.004	0.004	0.016	0.004
47	16	1.138	0.156	0.048	0.048	0.077	0.048
48	20	1.185	0.060	0.019	0.019	0.025	0.019
49	24	1.187	0.136	0.082	0.082	0.076	0.082
50	32	1.071	0.429	0.323	0.323	0.360	0.323
51	40	1.197	0.136	0.089	0.089	0.079	0.089
52	48	1.140	0.142	0.139	0.139	0.150	0.139
53	56	1.234	0.084	0.053	0.053	0.042	0.053
54	64	1.318	0.177	0.140	0.140	0.124	0.140
55	72	1.345	0.240	0.101	0.101	0.141	0.101

الخلاصة

هذا البحث يهتم بدراسة الخواص الريولوجية للمحاليل المائية للبوليمرات. البوليمرات المستخدمة في البحث هي : XC - بوليمر , كاربوكسي مثيل سيليلوز (نوعين) , هايدروكسي مثيل سيليولوز , بولي فنيل الكحول.

تم دراسة الخواص الريولوجية باستخدام جهاز (Fann VG-35A) وذلك بقياس اجهاد القص (shear stress) المصاحب لكل معدل قص (shear rate) . تم اجراء 55 تجربة بتراكيز مختلفة وعند درجة حرارة 30 °م (± 1 °م).

تم استخدام برنامج مايكروسوفت ايكسيل لايجاد افضل نموذج رياضي يمثل النتائج العملية . وقد وجد بان النموذج رياضي الاسي (Power law) هو الافضل .

من خلال النتائج العملية وجد بانه كلما زاد تركيز البوليمر في المحلول فان دليل سلوك الجريان n يقل , و هذا التصرف يعكس الحقيقة بانه كلما زاد تركيز البوليمر فان المحلول يتجه اكثر نحو المحاليل اللانيوتينية. تم ايجاد المعادلات الرياضية التي تبين تاثير التركيز على n (معادلة لكل بوليمر مستخدم).

كذلك من خلال النتائج العملية وجد بانه كلما زاد تركيز البوليمر في المحلول فان دليل التماسك k يزداد , و هذا التصرف يعكس الحقيقة بانه كلما زاد تركيز البوليمر فان المحلول يصبح اكثر سمكاً و لزوجة. تم ايجاد المعادلات الرياضية التي تبين تاثير التركيز على k (معادلة لكل بوليمر مستخدم).

اخيرا وجد بان محاليل XC بوليمر لها لزوجة اكثر من بقية محاليل البوليمرات المستخدمة و بان محاليل XC بوليمر تقل لزوجتها اكثر عند تعرضها لمعدلات قص.

شكر و تقدير

أود ان اعبر عن خالص شكري و تقديري وامتناني العميق للمشرف الدكتور **مهند عبد الرزاق** لما قدمه لي من توجيهات قيمة طوال فترة انجاز البحث .

أود ايضاً ان اتوجه بالشكر الى رئيس قسم الهندسة الكيمياوية الأستاذ الدكتور **قاسم جبار السليمان** لارشاداته ونصائحه السديدة .

ولا أنسى ان اتقدم بالشكر و الامتنان الى من لازمني طوال فترة البحث وخلال اصعب الظروف الى أعز من في الوجود الى **أمي** و **أبي** و **أخواني** و **أخواتي** .

أريج جاسم محمد

تأثير تركيز البوليمرات في المحاليل المائية على الخواص الريولوجية

رسالة
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وهي جزء من متطلبات نيل درجة ماجستير علوم
في الهندسة الكيمياوية

من قبل

أريج جاسم محمد

(بكلوريوس علوم في الهندسة الكيمياوية 2005)

جمادى الثاني 1429
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