THE INFLUENCE OF MECHANICAL EFFECTS ON DEGRADATION OF DRAG REDUCING AGENTS

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by

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Abstract

Mechanical shear degradation hampers the practical usage of polymers for turbulent drag reduction application. Mechanical degradation refers to the chemical process in which the activation energy of polymer chain scission is exceeded by mechanical action on the polymer chain, and bond rupture occurs. The mechanical degradation of high molecular weight Polyisobutylene polymers (Oppanol B) was studied by exposing there dilute solutions to high mechanical stirring (1200, 1500 and 1800 rpm). Three Oppanol B, 150, 200 and 250 types of molecular weight, 2.5, 4.1 and 5.9million g/mole were considered in present work. The shear viscosity of Oppanol B stock solutions of concentrations, 0.5, 1.0 and 1.4w/v% was measured as function of exposure time.

It has been found that the extent of the degradation is a function of the molecular weight, stirring speed and concentration. Therefore, polymer chains having different molecular weights show different time dependent resistance by exposing there solutions to mechanical stirring. It was observed, that the degradation efficiency of higher molecular weight is larger than that of lower molecular weight in a whole polymer concentrations, and stirring speeds. Thus, the highest molecular weight Oppanol B was more susceptible to stirring degradation accompanying more molecular weight lowering.

The drag–reduction efficiency which has been studied for dilute solutions of Polyisobutylene (Oppanol B types) with the three molecular weight mentioned above, in a laboratory circulation turbulence flow loop. The time dependence drag–reduction data was compared with

the observation of shear degradation by stirring behavior. The decrease of drag reduction with time is in evident to the mechanical degradation observed by shear stirring and viscosity decline of polymeric additives.

Xanthan Gum (XG) have been tested for its drag-reduction performance, shear stability and degradability. 0.5 and 1.0w/v% solutions were also exposed to shear stirring at different speeds (1200, 1500 and 1800rpm) and time(4hr). It has been noticed by measuring the viscosity changes, that XG solutions show more shear stability than Oppanol B polymers. The viscosity lowering was noticeably low at exposure time up to 4hr.

Xanthan gum agent was tested for its drag-reduction effectiveness at concentrations up 200ppm and different flow rates in turbulent water flow circulation system. XG as a rigid polysaccharide shows relatively poor drag-reducing agent. It requires much higher concentrations, 200ppm to cause an expected drag reduction about 19%, compared to around 50ppm for Oppanol B 250 additive operating at similar flowing conditions.

The time dependence drag-reduction effectiveness experiments indicate that XG additive exhibit more shear stability than of Oppanol B as flexible polymers in turbulent pipe flows. This observation is also in evidence to that noticed by shear stirring degradation results.

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Notations

Variable Notations

Symbols		Notations	Unit
A	=	Area	[m^2]
C, c	=	Polymer concentration	[g/ml, ppm]
D	=	Pipe diameter	[m]
%DR	=	Percentage drag reduction	[−]
ID	=	Inside diameter	[m]
K	=	Mark–Houwink parameter	[cm^3/g]
M, Mw	=	Molecular weight	[g/mole]
$\overline{M}_n$	=	Number average molecular weight	[g/mole]
$\overline{M}_W$	=	Weight average molecular weight	[g/mole]
Δp	=	Pressure drop	[N/m^2]
Δp_{dr}	=	Pressure drop with drag reducer agents	[N/m^2]
Q	=	Volumetric flow rate	[m^3/hr]
Re	=	Reynolds number	[−]
t		Time	[min, hr]
u	=	Fluid velocity	[m/s]
w/v	=	weight of polymer/volume of solvent	[g/ml]

Abbreviations

CDR = Conoco Drag Reducer

CMC = Carboxymethylcellulose

DR = Drag Reduction

DRA = Drag Reduction Agent

GG = Guar Gum

GPC = Gel Permeation Chromatography

HEC = Hydroxyethylcellulose

PAM = Polyacrylamide

PCIP = Polycisisoprene

PDMS = Polydimethylsiloxane

PEO = Polyethylene Oxide

PIB = Polyisobutylene

PMMA = Polymethylmethacrylate

ppm = Part per million

PS = Polystyrene

RDA = Rotating disk apparatus

rpm = Revolution per minute

% RV = Percentage viscosity reduction

TAPS = Trans Alaska Pipeline System

XG = Xanthan Gum

Greek Letters

ρ = Density [g/cm^3]

η, μ = Dynamic viscosity [centipoises]

$[\eta]$ = Intrinsic viscosity [cm^3/g]

α = Mark-Houwink parameter constant [–]

η_{sp} = Specific viscosity [–]

η_o = Viscosity of pure solvent [centipoises]

Subscripts

0 = at time =0

dr = with drag reducer agents

sp = Specific

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Chapter One

Introduction

1.1 Introduction

A large amount of energy loss due to friction occurs in many cases of turbulent flow, generally. However, it is well known that turbulent drag reduction (DR) which is drastic reduction of frictional resistance can be easily observed by dissolving a minute amount of long–chain polymer molecules in water or in organic solvents in a turbulent flow(1). Polymer solutions undergoing a turbulent flow in a pipe thereby require lower pressure drop to maintain the same volumetric flow rate. The addition of small amounts of additives to the flowing fluids can show significant effects on a lot of flow, transition to turbulence, vortex formation and break-up(2). To compensate for the loss of energy due to friction pressure, additional energy must be consumed. Consequently, a decrease in friction loss would allow lower energy consumption or alternatively an increase in flow rate under the original pumping conditions(3).

Effective polymeric drag reducing additives are considered to be flexible, linear with a high molecular weight(4) such as Polyethylene oxide (PEO) and Polyisobutylene (PIB). The dependence of drag reduction efficiency is a function of polymer molecular weight, polymer concentration, pipe diameter and the degree of turbulence. However, the usage of these polymers is limited because of their susceptibility to flow induced shear degradation(5).

The degradation of polymers by mechanical action is a depolymerization reaction in which the activation energy is supplied by the mechanical action on the polymer. This phenomenon has been known for some time and has been widely used in the rubber processing industry to make the raw rubber easier to work by reducing its molecular weight. The use of high polymers as drag–reducing agents in turbulently flowing liquids focused attention on the degradation of polymers(6).

Degradation reduces the effectiveness of polymer additives because of the strong dependence of effectiveness on molecular weight(6). An additives demonstrated a desirably high drag reduction efficiency when undesirable mechanical degradation under turbulent flow occurs. Therefore, molecular degradation is one of the major defects in the drag reduction application, since the polymeric additives are exposed to strong turbulent elongation strain and shear stresses. The mechanical degradation is assumed to be that the polymer chains can indeed the fully extended by turbulent flow and experience the chain midpoint scission of macromolecule(7). The mechanical degradation of high molecular weights polymers such as PEO and PIB under turbulent flow was investigated at various conditions of temperature, polymer concentration, and rotation speed. Since the long chain polymer having different molecular weights will show different time dependent resistance. In other words, longer molecules are more susceptible to mechanical degradation, accompanying more rapid degradation(8).

1.2 Aim of the present work

1. The present work deals with the experimental data for mechanical degradation and the performance of drag reducing polymers. Dilute solutions of Polyisobutylene with three molecular weights and Xanthan gum were exposed to shear degradation using mechanical stirrer with blades.
2. Relations between the decrease in drag reduction effectiveness of Polyisobutylene and Xanthan gum with time in a closed re−circulation loop were studied.

Chapter Two
Literature Survey

2.1 Drag reduction phenomenon

It is well known that the addition of small amount of polymer to a turbulent Newtonian fluid flow can result in a drag reduction. Drag reduction in polymer solutions is the phenomenon whereby extremely dilute solutions of high molecular weight polymers exhibit frictional resistances to flow much lower than the pure solvent. Although applications are beginning to appear, the principal interest to date has been in attempting to relate the effect to the fluid mechanics of turbulence and turbulent flow(9). Since the early forties, drag reduction has become an increasing interest in science and technical applications. The phenomenon of drag reduction by polymer additives was first discovered by Toms B.A. in 1948(10). Toms discovered that adding small quantities of high molecular weight polymer to a Newtonian fluid in turbulent flow could considerably reduce frictional drag exerted by the fluid when it flow over a surface such as pipelines. The most striking application of this behavior is reduction in pumping energy requirements for pipelines flow. Drag reduction not only important from an application point of view but also from a fundamental view point(11). Research interest in aqueous and hydrocarbon fluids intensified in the 1960s and 1970s. One of the earliest commercial applications was the use of water – soluble polymers in fire–fighting equipment(12).

The first major application of drag reduction in oil pipelines has been in the Trans Alaska Pipeline (TAP)$^{(13)}$. That in some cases, it is necessary to increase the transported liquid flow rate in built pipelines to avoid any extra costs and time spend on building new pipelines to have the same flow improvement needed. So, drag reducers were used to overcome this problem. The DR has also industrial applications can be found in many areas such as transport of crude oil$^{(14)}$, sewage systems to prevent overflowing after heavy rain$^{(15)}$, transportation of solid particle suspensions$^{(16)}$and firefighting to increase the range of water jets, and water supply and irrigation systems$^{(17)}$. It is used also in medical application by addition low concentration of polymers that might be capable of improving blood flow through stenotic vessels without altering flow through normal vessels as was suggested by a study by Unthank et al$^{(18)}$.

The quantitative definition of the phenomenon of drag reduction is given below as merely a comparison of the pressure loss with and without the presence of a chemical DRA$^{(19)}$.

$$\%DR = \frac{\Delta p - \Delta p_{dr}}{\Delta p} * 100 \qquad \ldots(2.1)$$

The effect of drag reduction is to reduce the friction to a value considerably lower than the turbulent flow of the solvent but not approaching that corresponding to laminar conditions. Typical drag reduction fall between solvent values for laminar flow and the curve for turbulent flow as shown in figure (2.1)$^{(9)}$.

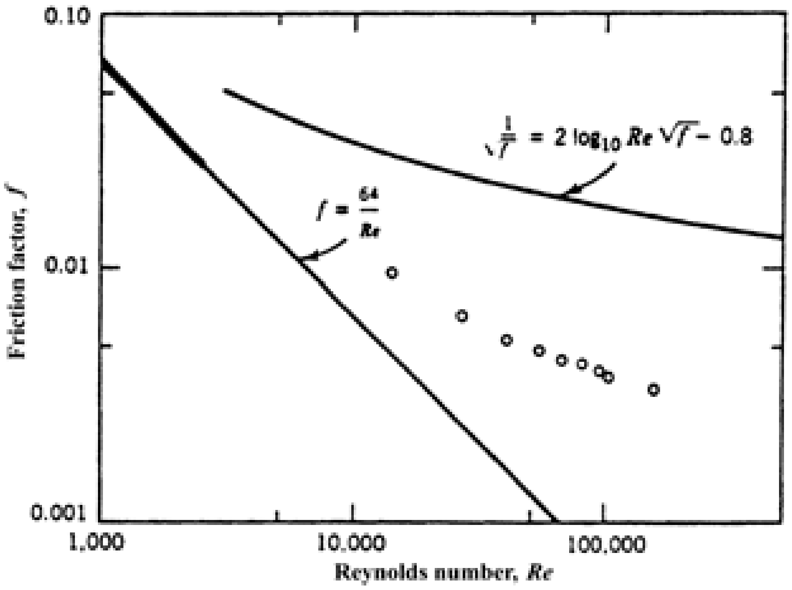


Figure (2.1) Typical data for drag reducing polymer solutions[(9)]

The addition of drag reducing additives is done by two different methods resulting in two different types of drag reduction, homogeneous and heterogeneous. Dissolving the polymer in the fluid before the experiment takes place is in the case of homogeneous DR. While by injection of moderately concentrated polymer into turbulent pipe flow results in a heterogeneous DR[(20)].

Two principal theoretical concepts have been put forward to explain the phenomenon of drag reduction by polymers. The first can be attributed to Lumley [(21,22)], who proposed a mechanism based on the extension of the polymers. Lumley postulated that stretching of randomly coiled polymers, primarily in regions with strong deformations such as the buffer layer, increases the effective (extensional) viscosity. Lumley also mentioned that the influence of the polymers on the turbulence only becomes important when the time scale of the polymers (e.g. the relaxation time) becomes larger than the time scale of the flow, which is known as the onset of drag reduction. The second theory, attributed to de Gennes, is that drag reduction is caused by the elastic rather than the viscous properties of polymers. This idea is supported by experiments showing that drag reduction also occurs when the polymers have been injected in the centre of the pipe(23).

2.2 Factors effecting on DR

The dependence of drag – reduction efficiency is known to be a function of polymer concentration, polymer molecular weight, degree of turbulence, pipe diameter and solvent type(5).

2.2.1 Polymer concentration

Percentage drag reduction increases as the concentration increases due to the increase in the number of available drag reducers. However, as the polymer concentration increases further, the solution viscosity drastically increases, leading to a decrease in the turbulent strength, i.e., reduction of Reynolds number and an increase in the frictional drag(24). Furthermore, the effect of concentration on %DR is variable according to the nature of polymer. The flexible polymers like Polyethylene oxide and Polyacrylamide, which are synthetic polymers, cause maximum drag reduction (≅80%) in turbulent pipe flow at a concentration of few ppm. On the other hand, rigid polysaccharides, from natural resources, like Guar gum, Xanthan gum, Carboxymethyl cellulose, require much higher concentration ≥500 ppm to cause maximum drag reduction (≅60%)(25). A typical relationship between DR and Polyethylene oxide (PEO) concentration at a Reynolds number of 14000 in a small pipe which indicate a flow in the turbulent region shown in figure (2.2)(9).

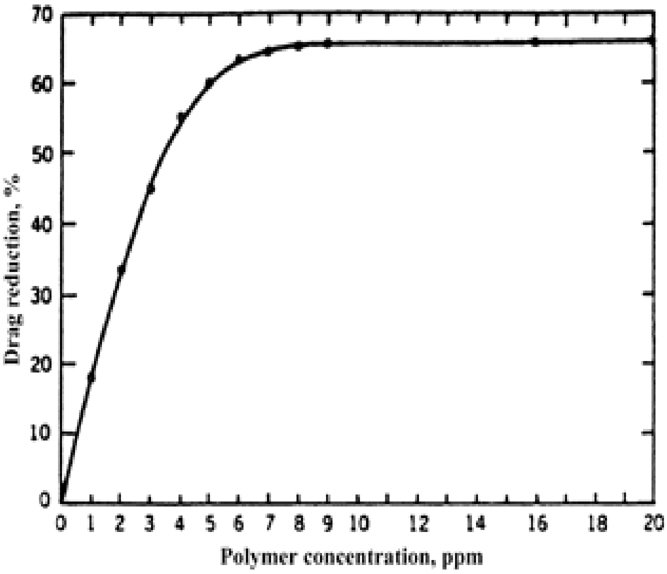


Figure (2.2) Drag reduction of (PEO) in water at Reynolds number of 14000, in small pipe(9)

2.2.2 Polymer molecular weight

Effective polymeric drag – reduction additives are considered to be flexible, linear with a high molecular weight(4). The polymer with high molecular weight about 10^6g/mole is more effective as a drag reducer. While, polymer with a molecular weight below 100000 seems to be ineffective. As the average molecular weight of Polyethylene oxide (PEO) is increased from $2*10^5$ to above $5*10^6$g/mole, the solution concentration to achieve about 70% drag reduction on a rotating disk is reduced from 600 to 100ppm. In other words, the higher the molecular weight, the greater the drag reduction for a given concentration and Reynolds number. The longer polymer chain provides more chance for entanglement and interaction with the flow. It has been confirmed that the extension of the polymer chain is critical for drag reduction. The most effective drag reducing polymers are essentially in linear structure, with maximum extensively for a given molecular weight. Polyethylene oxide, Polyisobutylene and

Polyacrylamide are typical examples of linear polymers. Polymer lacking linear structure, such as gum arabic and the dextrans are ineffective for drag reduction(26). Turbulent drag reduction with PEO in a Rotating Disk Apparatus (RDA) was investigated with different molecular weights. The DR efficiency of higher molecular weight is larger than that of lower molecular weight in a whole polymer concentration range up to 250ppm(27). Three polymers with different molecular weights ranging between 2.5 to about 5.9 million g/mole had been studied. It was found that friction factor decreased dramatically by increasing the molecular weight, which resulted in more increase of drag reduction(28).

2.2.3 Degree of turbulence

It is well known, that the drag–reduction phenomenon works in turbulent flow(29). Therefore the degree of turbulence has a predominant effect on its effectiveness. The use of Reynolds number based on the solvent viscosity provides a direct indication of the degree of drag–reduction, which is defined as a reduction in pressure drop due to the same flow rate, i.e., the same solvent Reynolds number. The percentage drag–reduction increase with Reynolds number increase (flow rate increase)(24). This behavior agrees with Berman and his workers(30,31), who reported, that an increase in Reynolds number leads to an increase in the strain rate and a decrease in the time scale. Then the elongation reached a constant level for a given solution. Moreover, these polymer threads have a high viscoelasticity and they may cause an interaction with turbulent eddies and consequently, a remarkable drag–reduction was observed.

2.2.4 Diameter of pipe

One of the most interesting factors in the study of the drag reducing fluid is the diameter effects. It is well known that the drag reduction effectiveness of polymers decreases with increasing diameter(24,28). Virk et.al(32) concluded that the frictional drag reduction included by a given concentration of polymer decreases with increasing the pipe diameter. Burger et.al(13) conducted experiments in the TAPS pipeline (Trans Alaska Pipeline) using drag reducing additives. They concluded that drag reduction was increased with decreasing diameter, increasing velocity and decreasing viscosity. Mansour et.al(33) had studied the effect of diameter for Iraqi and Saudi crude oils and they concluded that drag reduction increase with increasing pipe diameter. This agrees with the works of Berman, who found that in a large pipe, where the persistence time of the strain field as a higher, drag reduction increased, compared with a small pipe size. Robert et.al(34) showed that, the small pipe results indicated lower % drag reduction as compared with large pipes.

2.2.5 Type of solvent

Polymers are more efficient drag reducer in a good solvent than in a poor solvent. The effect of polymer–solvent interactions or the nature of the solvent on the extent of drag reduction were studied by comparing pressure drop measurements of solutions of PIB L–80 in a good and in a poor solvent. Cyclohexane at 25^0C is a good solvent for PIB and polymer–solvent contacts leading to expanded conformations of polymer molecules in solution. Benzene at 24^0 C is a poor solvent for PIB. Thus, for approximately equal concentrations of the same polymer, considerably more drag reduction is obtained when the molecules have expanded rather than unexpanded conformations(29). The performance of polymeric drag reducers in a variety of crude oils seems to vary quite substantially with greatest effectiveness being found in the low viscosity crude oils such as Kirkuk crude oil of the Middle East. The variability in performance in crude oils is primarily a function of the viscosity of the crude, as well as polymer chemical composition(19).

In a poor solvent, the polymer molecules are attracted to each other more than to solvent molecules so that intermolecular contact might be more productive of entanglement than in a good solvent(35). Polymer chains are more extended and thus have larger intrinsic viscosities in good than in poor solvents(36). A work had been done by Conoco. It was concluded that lighter crude oil causes higher %drag–reduction than heavier crude by using Conoco Drag Reducer (CDR) additive as illustrated in figure (2.3)(24).

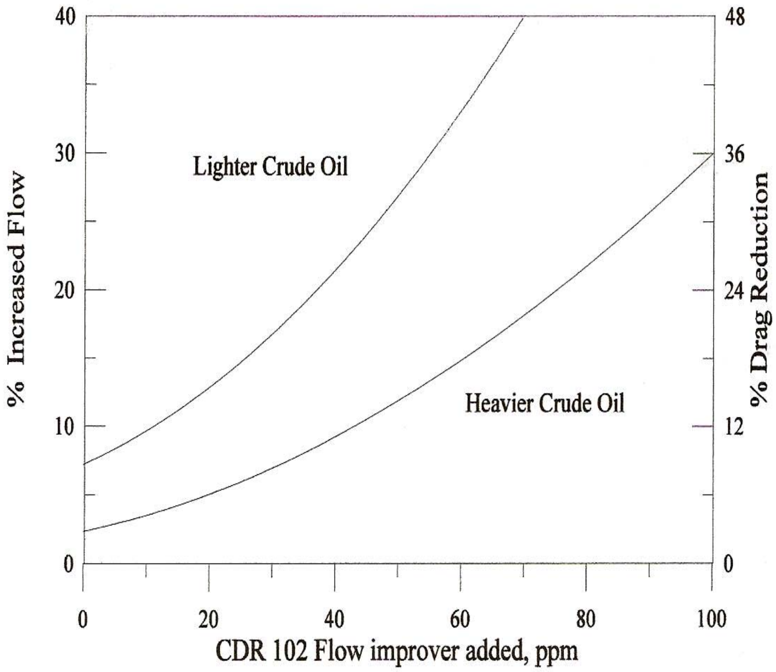


Figure (2.3) solvent type effect on % drag reduction and % flow increase(24)

2.3 Additives

In the past several decades, there had been a remarkable growth in the use o f additives to facilitate the transportation of fluids in the pipes. These additives are able to substantially reduce the frictional loss associated with turbulent flow of fluid(19). By lowering the energy loss, those additives allow the pipeline fluid to move faster at any working pressure so that more fluids can pass through the line without mechanical expansion. Also additives can produce substantial decreases of the frictional pressure drop of fluids in turbulent flow when injected at concentrations of just a few parts per million(12). Additives are effective only when the flow is turbulent. When a DRA is dissolved in a solvent, it produces a solution which in laminar flow has the same pressure drop, and therefore has the same Newtonian viscosity as the solvent. While when the solution is in turbulent flow, a DRA produce a pressure drop smaller than that which would occur with untreated solvent moving at the same flow rate(37).

Additives are highly viscoelastic and thixotropic. They may have high viscosity at low shear rates while having low viscosity at higher rates. The viscosity is affected by temperature and increases with decreasing temperature. DRA–solvent solutions are viscoelastic, time dependent, shear degradable, non–Newtonian fluids. The effectiveness of DRA depends to a certain extend on the viscosity of the untreated oil and decreases as viscosity increases(37). The most serious problem in the effectiveness of drag reducer is the chain degradation of polymer by shear strain in turbulent flow. Ultra high molecular weight polymers are more susceptible to shear induced degradation, and polymers with linear chain structure are more vulnerable than branched polymers.

Various drag reducing additives are available which can be classified: high molecular weight, linear and flexible polymers, surfactants, and suspended particles.

2.3.1 Polymers

Polymers are long chain molecules when added in dilute concentrations to fluids, they reduce friction drag in pipes by as much as 20% - 80%. The origin of the drag reduction mechanism is the stretching of polymer molecules in a turbulent flow. This stretching dampens turbulent fluctuations and reduces the drag. Thus, the extent of drag reduction is a function of the size of the polymer, governed by its molar mass and the number of polymer molecules, governed by the polymer concentration(11). The most effective drag reducing polymers are essentially of linear structure, long chain, good solubility and high molecular weight. Typical molecular weights for drag reducing polymers range from 1 to 10 million, with higher molecular weight polymers giving better drag reduction performance(38). Table (2.1) summarizes the main drag reducer polymers(39).

Table (2.1) Drag reducer polymers (39)

Water soluble	Hydrocarbon soluble
Polyethyleneoxide (PEO)	Polyethyleneoxide (PEO)
Polyacrylamide (PAM)	Polymethylmethacrylate (PMMA)
Sodium Carboxymethylcellulose (CMC)	Polystyrene (PS)
Guar Gum (GG)	Polydimethylsiloxane (PDMS)
Xanthan Gum (XG)	Polyisobutylene (PIB)
Hydroxyethylcellulose (HEC)	Polycisisoprene (PCIP)

Polyethyleneoxide (PEO) has been the most widely studied for both laboratory and commercial applications including fire fighting and marine propulsion. PEO is flexible, linear with a high molecule weight, its utility in multiple pass application is limited due to its extreme sensitivity to shear degradation. Drag reduction similar to that obtained in water has been shown for PEO in other solvents such as, sea water, plasma, benzene, dioxane, and chloroform. Mixed PEO system such as PEO graft polymer, polymer /soap and polymer/dye mixtures have shown to provide varying levels of drag reduction(40).

Polyacrylamide (PAM) is the other synthetic water soluble and differs from PEO in that it has a side chain and is less susceptible to shear degradation. The related polymer, polyacrylic acid can be formed by hydrolysis of PAM. Most of the laboratory and commercial studies, however, have focused on PEO and PAM due to their availability, and their relatively low cost (40).

Sodium carboxymethylcellulose (CMC) is a water soluble, white color, odourless and non-toxic powder. It is consider as an anionic polymer. Three grades of CMC are available, low viscosity, medium viscosity, and high viscosity. The viscosity of CMC solutions decreases and increases reversibly with the raising and lowering of temperature, but no permanent change occurs unless the solutions are kept at high temperature for a considered length of time. CMC suspensions are shear thinning they have high apparent viscosity at very low shear rates(41). Most solutions of CMC are pseudo plastic, that is the measured viscosity decreases with increase in shear rate. The viscosity not only depends on the shear history, but also on the time after shearing when the viscosity is measured. CMC is probably used in more varied applications than any other water soluble polymer today. CMC is used in the production of worldwide detergents, textiles, food, coating and cosmetics(42).

One of the most widely used commercial drag reducing biopolymer is guar gum (GG) which is a plant polysaccharide with a semi rigid backbone. It has been used for a number of years in oil field applications, and in the petroleum industry where its friction reducer agent was discovered(43). The major limitation of guar gum in drag reduction application is its susceptibility to biodegradation. It has been shown that resistance to shear and biodegradation can be increased by grafting acrylamide to guar gum molecules(44).

The other biopolymer which has been widely used as a commercial drag reducer is Xanthan gum (XG). XG is an intracellular polysaccharide produced by the bacteria xanthommnas. XG is a long chain polysaccharide composed of the sugars glucose, mannose, and glucuronic acid. The backbone is similar to cellulose with added side chains of trisacharides (three sugars in a chain)(45). XG is a white to cream colored free flowing powder soluble both in hot and cold water but insoluble in most organic solvents. Even at low concentration XG solutions show a high degree of viscosity in comparison with other polysaccharide solutions. This property makes it a very effective thickener and stabilizer. XG solutions are highly pseudo plastic but not thixotropic even after high shear rates the initial viscosity is rebuilt instantaneously(46). Kenis has demonstrated greater shear stability for XG than for a number of other drag reducing molecules. The shear stability and resistance to shear degradation decreased as follow: PAM > XG > PEO > GG(47).

Polymethylmethacrylate (PMMA) is the synthetic polymer of methyl methacrylate. PMMA is thermoplastic that is hard and stiff but brittle. It has good abrasion and UV resistance and excellent optical clarity but poor low temperature, fatigue and solvent resistance(48).

Polystyrene (PS) is anionically polymerized polystyrene of a molecular weight about $1.5*10^6$ was used also as drag reducer additive. The polydispersity index ($PI=\overline{M}_w/\overline{M}_n$) was 1.05. Here, $\overline{M}_w$ and $\overline{M}_n$ are the weight average and number average molecular weight respectively. The suitable solvents for PS additive are pure chloroform, benzene and toluene(49).

Polyisobutylene (PIB) is a synthetic rubber is a linear polymer of varying average molecular weights. It is chemically inert and therefore possesses excellent resistance to oxidative and thermal degradation(50). Polyisobutylenes are highly olefin hydrocarbon polymers composed of long straight chain macromolecules containing only chain–end olefin bonds. This molecular structure leads to solubility in hydrocarbon solvents. Polyisobutylenes are light colored, odorless, tasteless and nontoxic. Polyisobutylene of high molecular weight, such as Oppanol B types, are tough elastic solids. They are highly resistant to penetration by water vapor and gases, and often are added to other polymers to reduce their permeability. The higher the molecular of PIB is the lower its permeability. PIBs are stable under normal conditions of use but they can be degraded by heat, mechanical shear (high speed stirrer), ultra violet radiation and some chemicals such as organic peroxides(38). PIB of high molecular weight can used as viscosity improvers additives in motor oils. A small amount of this polymer dissolved in a motor oil greatly reduces the decrease in viscosity of the base oil at high temperatures and the increase in viscosity at low temperatures(51).

2.3.2 Surfactants

Surfactant (surface active agent) solutions also used as additives in drag reduction. The mechanism with these additives is possibly similar to that occurring in polymer solutions. Although these agents have low molecular weights, they seem to form long chain agglomerates or micelles. At high stresses, the micelles bonds are broken and the drag reduction effect disappears. If the shear stress is reduced, the micelles reform, in contrast to polymer solutions, and the original drag–reducing effectiveness is regained(9). The disadvantage of this type of additives is that the surfactant drag reducing additive require higher concentration if it is compared with high molecular weight polymeric additives.

Surfactant solutions with rod–like micelles show remarkable viscoelasticity and the effective drag reduction in a turbulent pipe flow has been reported by many investigators(54,55,56). The known surfactants as drag reducer are the quaternary ammonium salt cationic surfactants, such as cethyltrimethylammonium chloride and stearyltri methylammonium chloride. Sodium salicylate (NaSal) is added as counter–ion. The amount of NaSal is usually adjusted to the same wt% as that of the surfactant additive(56).

2.4 Degradation of polymers

2.4.1 Introduction

The usage of polymers as drag–reducers is limited due to there molecular degradation(5). Polymer degradation is characterized by an uncontrolled reduction in the molecular weight of the polymer.

Degradation is a deleterious process. To degrade a polymer is to impair it in respect to some physical property or to reduces its complexity in which the activation energy of polymer chain scission is exceeded by the mechanical action on the polymer chain thus bond rupture occur. Since degradation is a chemical process it affects not only the chemical composition of the polymer but also various physical parameters such as chain conformation, molecular weight distribution, crystallinity, chain flexibility, crosslinking, branching, etc. Different polymeric materials exhibit wide variation in their response to degradative agents depending on their chemical composition and structure, size, shape. Therefore there are many factors that contribute to the resistance (or susceptibility) of polymers towards various degradative agents(57).

Polymer degradation is broadly of two types, those are:
(i) Chain end degradation
(ii) Random degradation
In the first type the degradation starts from the chain ends resulting in successive release of the monomeric units. For this reason this type of degradation is also called "depolymerisation". The result is that the molecular weight of the polymer decreases slowly and a large quantity of the monomer is librated simultaneously. The second type of degradation occurs at any random point along the polymer chain instead of at the chain ends. Here, the

polymer degrades to lower molecular weight fragments but (unlike in chain–end degradation) practically no monomer is librated(58).

Degradation of polymers may be brought about either by physical factors, such as heat, light or mechanical stress or by chemical agents, such as oxygen, ozone, acids or alkalis(58). We can prevent degradation by avoiding high speeds in stirring or transporting polymers solutions; using the highest temperature possible commensurate with prevention of thermal degradation and using good solvents (those with high intrinsic viscosity) of low viscosity(35).

2.4.2 Mechanical degradation

Mechanical degradation refers to the chemical process in which the activation energy of polymer chain scission is exceeded by the mechanical action on the polymer chain and bond rupture occurs. There have been numerous investigations on the mechanical degradation of both dilute and concentrated polymer solutions which show conflicting results depending on the experimental conditions such as laminar and turbulent flow, polymer concentration range and solvent nature effect(7,36,59-65).

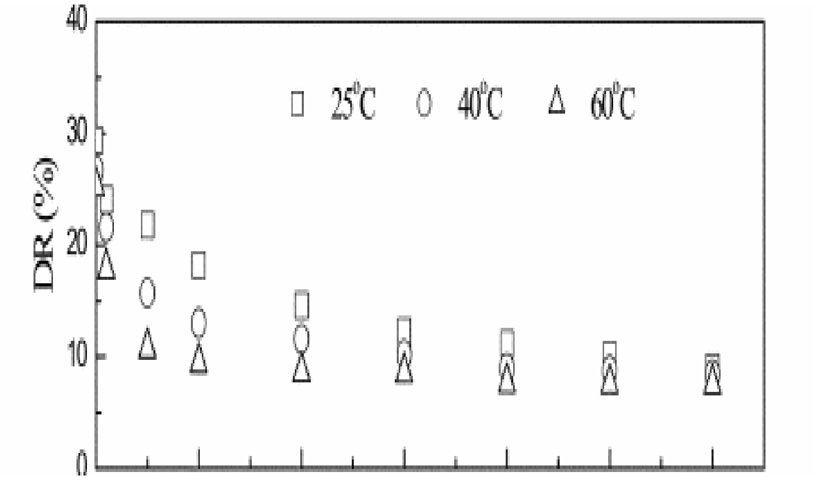
Mechanical shear degradation has been encountered in various practical situations such as the use of polymer for turbulent drag reduction and as viscosity enhancers in motor oils(61). Many mechanical shear degradation experiments have been performed under turbulent flow conditions(49). A simple compound such as water or benzene cannot be broken up by subjecting it to mechanical stresses such as high speed stirrer. While a polymer such as polystyrene, dissolved in a solvent when subjected to stirring, undergoes considerable molecular degradation. In fact in the rubber industry, rubber is masticated by passing it through two rotating rollers to reduce its molecular weight and make it more processable. Many interesting observations have been made by researchers on mechanical degradation. For instance the bigger molecules are found to be affected much more than the smaller ones during mechanical degradation. This mean the larger the initial molecular weight the greater the molecular weight drop due to mechanical degradation(58).

Polymers are continuously subjected to deformation, especially in the pump which cause the scission of the polymers. If a centrifugal pump is used the higher molecular weight polymer will be degraded rapidly due to its exposure to high mechanical shear. Whereas using the gear pump reduces the polymer degradation(24).

2.4.3 Thermal degradation

Thermal degradation of polymers is molecular deterioration as a result of overheating. At high temperatures the components of the long chain backbone of the polymer start to separate molecular scission and react with one another to change the properties of the polymer. The chemical reactions involved in thermal degradation lead to physical and optical changes relative to the initially specified properties. Thermal degradation generally involves changes to the molecular weight, molecular weight distribution and colour(66). Thermal degradation of polymer may follow either chain end or random degradation. The end chain mechanism gives the pure monomer while random degradation lead to the formation of a host of products depending on the structure of the polymer. Since many polymers have a carbon–carbon (c–c) chain as the backbone, their thermal stability is dependent on the stability of c–c bond(58).

The effect of thermal degradation on turbulent drag reduction efficiency was studied for Polyethylene oxide with two different molecular weight. It was found that the susceptibility of PEO to degradation increase with increasing temperature. Figure (2.4) show the effect of temperature on percent drag reduction examined with 50ppm PEO(67).



Time (min)

Figure (2.4) Effect of temperature on effectiveness of PEO on drag–reduction(67)

2.4.4 Photo degradation

Degradation of photodegradable molecule is caused by the absorption of photons particularly those wavelengths found in sunlight, such as visible light and ultraviolet light (UV). However other forms of electromagnetic radiation can cause photo degradation. Photo degradation includes photo dissociation, the break up of molecules into small pieces by photons. It also includes the change of a molecules shape to make it irreversibly altered, such as the addition of other atoms or molecules(68). A number of substances are known which help to protect polymers against UV radiation. These appear to be work by absorbing the UV radiation at frequencies which are dangerous and re–emitting the energy at a lower frequency which is less damaging, such chemicals usually contain conjugated double bonds, benzene rings, and ketone groups which absorb ultra violet radiation and emit the energy as radiation in the visible spectrum. The rate at which this degradation occurs varies with the polymer. For example polystyrene(PS) degrades rather rapidly in sunlight, whereas polymethylmethacrylate (PMMA) is more resistant(69).

2.4.5 Degradation by high energy radiation

X–rays, alpha rays, beta rays and gamma rays are among the well known high energy radiations. Like UV rays, X–rays and gamma rays are electromagnetic radiations, but their energy level is much higher than that of UV rays. Beta rays are fast moving electrons and alpha rays are fast moving helium nuclei(58).

Degradation by the high energy radiations is more massive than that by the lower energy (UV) radiations. If the molecule is scissioned, the polymer degradation is associated with a reduction in the molecular weight. On the other hand crosslinking can take place between polymer molecules, building up the polymer network with a resultant increase in the molecular weight. Polymers which degrade on irradiation are such as, polyisobutylene, polytetrafluoro ethylene, cellulose, polymethylacrylate. On the other hand some polymers such as, polyethylene, polypropylene, polybutadiene, polyamides, polyacrylates, polyisoprene get cross linked when subjected to high energy radiations. Many polymers on being exposed to radiation give out gases such as H_2, CO_2, CO, CH_4, and NH_3. For example, polyethylene and polystyrene when subjected to high energy radiations give hydrogen. When, however, polyisobutylene is subjected to high energy radiations, methane and hydrogen are evolved(58).

2.4.6 Oxidative degradation

Oxidative degradation usually leads to hardening, discoloration as well as surface changes. The case of oxidative degradation of the polymer depends primarily on its structure. Thus unsaturated polymers such as polyisoprene or polybutadiene containing double bonds are easily attacked by oxygen. The mechanism of polymer oxidation is very complex and vary from polymer to polymer. Most researches on this subject has been directed towards the oxidation of hydrocarbon polymers. There are differences in mechanism between the oxidation processes of saturated and unsaturated hydrocarbons(69).

2.5 Review of degradation

Bestul(70) assumed that under conditions of constant rate of shear there exists a critical molecular weight polymer which will not be degraded. Any higher molecular weight polymer is degraded until it reaches the equilibrium value corresponding to the particular rate of shear.

Rodriguez and Winding(35) studied the degradation of polyisobutylene in a high speed stirrer and concluded that the rate of chain scission could be extrapolated to zero at zero concentration presumably because entanglements could not be formed.

Bueche(71) considered a randomly coiled polymer chain in shear field and concluded that it could not be stretched enough to cause breakage since the shear gradient would lead to rotation of the molecules. If the entanglements occurred, however he suggested that they would increase the force on the molecule with the greatest force occurring near the center of the chain.

Because the force depends on molecular size, Bueche΄s theory predicts that the higher molecular weight molecules will degrade more rapidly, with the degradation rate increasing as the square of molecular weight.

Boyd and Lin(72) proposed that degradation might occur randomly at any position along the polymer chain and showed theoretically that in this case the molecular weight distribution would tend toward the "most probable" distribution as ($\overline{M}_w/\overline{M}_n = 2$) as increasing amount of degradation took place.

Gadd(73) was one of the first researchers who investigated the phenomenon of polymer degradation by using solution of polyethylene oxide with a molecular weight of about $4*10^6$g/mole in addition to guar gum solution with concentrations not more than 60ppm. He supposed that the turbulence mechanically breaks up the long molecules so that they loss their effectiveness. On the other hand with guar gum solution little or no mechanical degradation seem to occur.

Patterson et.al(59) observed that the breakdown of small amounts of the high molecular weight fraction cause a decrease in the first normal stress difference and drag reduction for polyisobutylene (PIB) in two different solvents.

Porter et.al(74) observed a broadening of the molecular weight distribution to ($\overline{M}_w/\overline{M}_n = 2$) in experiments in which polyisobutylene was mechanically degraded in a concentric cylinder viscometer. Therefore, they concluded that Bueche΄s theory was incorrect in predicting the location of the breaks and they suggested that the degradation was random.

Metzner et.al(75) have shown that the velocity profile of a viscoelastic fluid is not blunt as it enters the tube due to the stretching flow that is developed external to the tube. In such a stretching flow locally high stresses on entangled molecules could cause degradation.

Patterson and Abernathy(76) studied the importance of the entrance effects on degradation in turbulent flow by using polyethyleneoxide solutions. They noted that a disproportionate amount of degradation occurred within the first 200 diameter of their test section. They also observed that tube entrance geometry had an effect on the amount of degradation in the entrance region, with a sharp edge tube producing more degradation than a bell mouth.

Culter et.al(77) explained the lack of an length to diameter ratio of capillary tubes (l/d) effect on the degradation of a polystyrene polymer which was not very viscoelastic by attributing the degradation to the high local stresses produced in the developing boundary layer in the entrance region.

Nakano and Minoura(36,60) observed that the rate of scission of polymer chain becomes greater in a good solvent than in a poor solvent at a low concentration by noting that the interaction between polymer molecules weakens at low concentrations. This fact suggested that the "stretching" and "entanglements" of polymeric chain affect the mechanical degradation.

Brostow and his coworkers(64,78,79) have developed a model from a statistical mechanical approach(78) and have investigated the validity of their model based on computer simulations. The %DR and mechanical degradation are related to macromolecular conformation in solution and the DR efficiency is proportional to molecular weight of polymer. The DR efficiency ratio is expressed as in equation (2.2)

$$DR(t) / DR(0) = M(t) / M_0 \qquad ...(2.2)$$

Where

DR(t) and DR(0) are the percent DR at time t and t=0 respectively

M(t) and M_0 are the effective number average molecular mass at time t and t=0 respectively.

He noted that the points on a chain where changes of direction occur are more vulnerable to chain scission. Depending on their specific location, some of them might be protected from degradation by their surroundings while others will undergo scission during flow.

Kim et.al(49) investigated the degradation of high molecular weight polystyrene under turbulent flow using a rotating disk apparatus for three different solvent systems at a maximum polymer concentration of 150ppm by weight. The solvents used were Benzene, Chloroform and Toluene. The drag reduction efficiency decreases with time due to mechanical degradation of the polymer molecules, and the extent of the degradation was found to be a function of solubility parameter of the solvents.

Sung et.al(67) studied the turbulent drag with polyethylene oxide of two different molecular weights in a rotating disk apparatus. The higher molecular weight PEO ($Mw=5*10^6$g/mole) showed less mechanical degradation than that of with a lower molecular weight ($Mw=4*10^6$g/mole) at the same concentrations. It was also found that susceptibility of the PEO degradation increases dramatically with increasing temperature.

Slaiman(24) investigated the time dependence of drag–reduction effectiveness for polyisobutylene, Oppanol type with three different molecular weights, namely 2.5, 4.1 and 5.9millions g/mole. A gradual decrease of percentage drag – reduction was observed as time progress, due to mechanical degradation of polymer molecules. The low molecular weight polymers are sharply degraded within the first 2hr, while the higher molecular weight polymer gradually degraded and it has shown a tendency to approach limiting value. He found also, that the extent of the degradation is higher in small pipe diameter compared with large diameters, due to increasing the fluid velocity in small pipeline.

2.6 Rheology of Polyisobutylene

Rheology is defined as the study of the change in form and the flow of matter, embrancing elasticity, viscosity and plasticity and how materials deform in response to outside forces. Rheological relationships are useful to understand the behavior of working fluids. For example a high viscosity liquid requires more power to pump than a low viscosity one. Knowing its rheological behavior, therefore is useful when designing pumping and piping systems(80). Rheological studies are most commonly applied to non–Newtonian fluids and gels to characterize viscosity as a function of shear rate, yield stress, elasticity and other fluid properties. A Newtonian fluid such water has a constant viscosity for any shear rate and no elasticity. The measurement of elasticity relies on polymer entanglement within the solution. However entanglement can occur because of large molecules or high concentrations and it can be difficult to discern which makes a greater contribution to rheological properties.

The rheological behavior of polymeric systems is profoundly influenced by their molecular weight and molecular weight distribution. The relationship between viscosity and shear rate is sensitive to polymer polydispersity especially in high molecular weight region. At low shear rates the viscosity is constant but when the shear rate increases above a certain value the viscosity begins to decrease with increasing shear rate(81).

Polyisobutylene is highly viscoelastic and thixotropic. The viscosity of PIB solution is somewhat affected by temperature and increases with decreasing the temperature(37). The Oppanol B types exhibit cold flow, which is dependent on the relative molecular mass. As a result of chain entanglements, the molecular network representative of Oppanol B with a high molecular weight is similar to that of rubber. The network is not held together by chemical bonds and yields under sustained loads as a result of chain disentanglement. Thus, Oppanol B with a high molecular weight behaves as a viscous liquid under sustained loads undergoes plastic deformation. PIB with a high molecular weight displays the viscoelastic behavior of a molten polymer. As the molecular weight increases Polyisobutylene becomes more and more similar to crosslinked natural rubber. At temperature above the glass temperature T_g, polyisobutylene with a high molecular weight is rubbery. The viscosity of high molecular weight polyisobutylene in various solvents differs decidedly owing to the difference in the degree of solvation. Aliphatic, aromatic, cyclic and halogenated hydrocarbon dissolve Oppanol B. The extent to which oppanol B is swollen by alcohols, ethers, esters and ketones increases with the length of the hydrocarbon chain. The rate at which Oppanol B is dissolved or swollen by homologous solvents is inversely proportional to the solvent's molecular weight(82).

There are many types of polyisobutylenes and they can be classified according to its molecular weight and its trade name. Several types of polyisobutylene are produced by BASF company in Germany and delivered under the marketing grade "Oppanol B " are listed in table (2.2)$^{(82)}$.

Table (2.2) Properties of high molecular weight Oppanol −B types$^{(82)}$

properties	Oppanol B type		
	150	200	250
consistency	Rubber like	Rubber like	Rubber like
Staudinger index(J_o) 0.001g/mole of solutions in isooctane at 20^{o}c	416-479	551-661	> 770
Volatile matter (150^{o}c,2 h) wt%	0.01	0.01	0.005
Glass temperature (^{o}c)	-61	-61	—
Weight average Mw (GPC) g/mole	2,500,000	4,100,00	> 5,900,00
Viscosity average (Mv) g/mole	2,600,000	4,000,00	> 5,900,00
Stabilizer content (ppm)	250-500	250-500	250-500
Ash content (ppm)	<100	<100	<100
Area of application	Sealants, adhesives, anti-misting	Drag reduction oil spills	Drag reduction oil spills

In common with most other high polymers, polyisobutylene with a high molecular weight is degraded by heat, oxygen, shear forces and ultra violet radiation; in other words, its average molecular weight is reduced by these agencies. Oppanol B 150 and 200 are stabilized with 2,6-ditert-butyl-4-methyl-phenol, which largely prevents degradation of the material during processing. When protected from light and moisture, Oppanol B 150 and B 250 can be stored for at least 1 year(82).

The high molecular weight and linear nature of PIB control the viscosity index in lubricant oils. At ambient temperatures, lubricants have relatively high viscosity. At engine operating temperatures about 90–200^{o}C, the lubricants tend to lose a substantial amount of there viscosities. The addition of polymeric index improvers increase high temperature viscosity. At ambient temperature polymeric viscosity improvers tend to be tightly coiled into spherical bodies without substantial contribution to viscosity. As the temperature increases, the polymer tends to uncoil and become extended in solution. This extended, more linear form increase viscosity in proportion to the degree of extension. Thus as the temperature increase the polymer contributes sufficient viscosity to the oil to maintain a adequate lubrication(83).

Viscosity is the measure of the internal friction of a fluid caused by molecular attraction which makes it resist a tendency to flow. The greater the friction the greater the amount of force required to cause the movement which is called shear. Shearing occurs whenever the fluid is physically moved or distributed as in pouring, spreading, mixing. Highly viscous fluids, therefore require more force to move than less viscous materials(80). The viscosity of dilute polymer solution depends on several factors namely the nature of the polymer and the solvent, the polymer molecular weight and concentration, the temperature and shear rate. Staudinger during the early 1930s used viscosity as a measure of the molecular weight of the polymer, to postulate his hypothesis about the long chain nature of polymer molecules. He proposed the relationship given in equation (2.3)(58).

$$\eta_{sp} = K_s c M \qquad \ldots(2.3)$$

Where

K_s = constant for a given polymer/solvent/temperature

c = concentration

M = molecular weight

η_{sp} = specific viscosity denoting the increase of viscosity of a polymer solution over that of the pure solvent according to the equation (2.4).

$$\eta_{sp} = (\eta - \eta_o)/\eta_o \qquad \ldots(2.4)$$

Where

η= viscosity of the polymer solution

η_o= viscosity of pure solvent

It can be seen from equation (2.3) that the specific viscosity is dependent on the concentration. In order to quantify a viscosity function of a polymer in a solvent, which will be independent of the concentration, the limiting value of reduced viscosity (η_{sp}/c) at infinite dilution is chosen and termed "intrinsic viscosity" [η] as given in equation (2.5).

$$(\eta_{sp}/c)_{c \to o} = [\eta] \qquad \ldots(2.5)$$

Standinger's equation was subsequently replaced by the famous Mark – Howink equation as shown in equation (2.6)(58).

$$[\eta] = KM^{\alpha} \qquad \ldots(2.6)$$

Where

K and α are constants for a given polymer/solvent/temperature system.

K and α values for some polymer/solvent system are given in table (2.3)(58).

Table (2.3) Mark−Houwink parameters for various polymers and solvents(58)

Polymer	Solvent	Temperature/°C	K (cm^3/g)	α
Polyisobutylene	Benzene	30	0.061	0.56
	Toluene	30	0.02	0.67
	Cyclohexane	30	0.0276	0.69
	Carbon tetrachloride	30	0.029	0.68
Polymethylmethacrylate	Acetone	30	0.0077	0.7
	Acetonitrile	30	0.0393	0.5
	Benzene	30	0.0052	0.76
	Toluene	30	0.007	0.71
Polycisisoprene	Toluene	30	0.002	0.728
Polyacrylamide	Water	30	0.0373	0.66
Polydimethylsiloxane	Toluene	30	0.0215	0.65
Hydroxyethylecellulose	Water	30	0.00948	0.87
Polyethylene oxide	Water	30	0.00875	0.79
	Benzene	30	0.0397	0.686

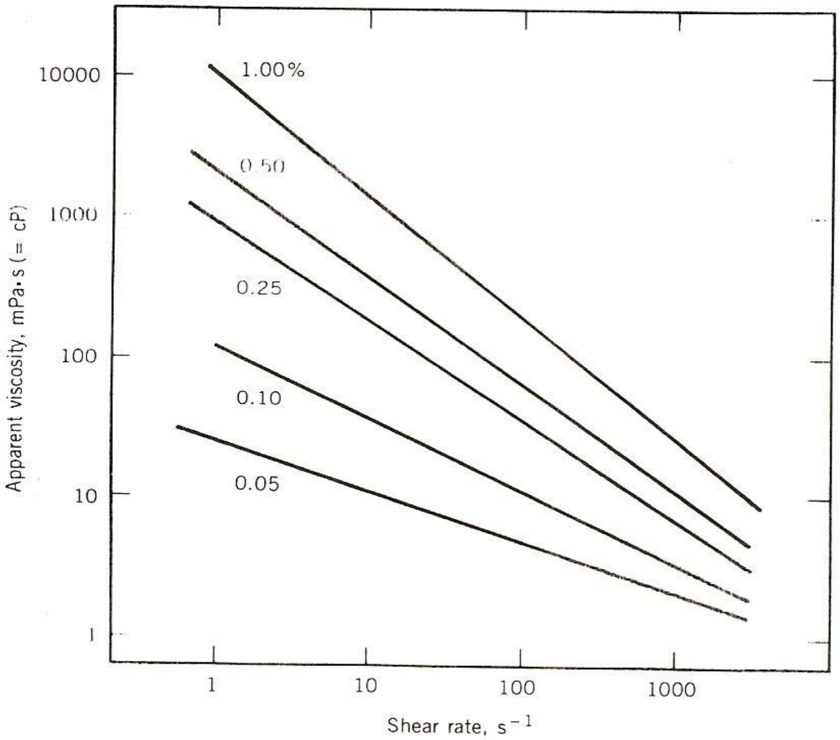
2.7 Rheology of Xanthan Gum

Xanthan gum solutions display high viscosity at low concentrations, high viscosity at low shear rates, a high degree of pseudo plasticity and high elastic modulus. When shear stress is applied, viscosity is reduced in proportion to the amount of shear. Upon the release of shear, total viscosity recovery occurs instantaneously. This behaviour of Xanthan gum solutions can be explained on the basis of the high molecular weight, rod like molecules, which forms complex molecular aggregates through hydrogen bonds and polymer entanglement. When the shearing force is removed the aggregates (junction zones) reassociate to produce high viscosity. This is the basis of pseudo plastic behaviour. Solutions of Xanthan gum have high apparent viscosity at low concentration and exhibit pseudoplastic rheology. The decreased apparent viscosity at high shear rates facilitates mixing, pumping, and pouring. High apparent viscosity at low shear rates stabilizes foams, emulsions and suspensions(84).

The effect of salts on viscosity depends on the concentration of the XG in the solution. At low gum concentration (below 0.3%) monovalent salts such as sodium chloride cause a slight decrease in the viscosity. The same effects occur with salts of most divalent metal (Ca and Mg). The degree of change in viscosity which occurs in formulated systems depends on pH. To develop optimal rheology and uniform solution properties, some type of salt should be present. Usually the salts naturally present in tap water are sufficient(84).

pH generally has very little effect on the viscosity of XG solutions. XG solutions maintain high viscosity over the pH range 2–12 with some reduction at extreme pH values. The change in viscosity with increasing temperature depends on concentration, pH, and shear rate. At high temperature viscosity is reduced, but even at elevated temperature XG solutions have excellent stability and upon cooling, essentially all viscosity returns. In other words XG solutions have excellent heat stability in the presence of salts, and viscosity reductions at high temperature are reversible upon cooling(84).

Viscosity and shear rate curves of Xanthan gum at different gum concentrations are shown in figure (2.5). The relative higher viscosity of XG at low shear rates and lower viscosity at high shear rates is indicated. This illustrates the potential for the use of XG at low concentration to produce solutions with high viscosity at low shear rates and therefore excellent suspension and emulsion stabilizing properties, low viscosity at high shear rates facilitates pumping(84).



Figure(2.5) Effect of shear rate on apparent viscosity (at 100 s^{-1}) at 25^{o}c for 0.05–1.00%(w/w) Xanthan gum(84)

Chapter Three

Experimental Work

3.1 Materials

The hydrocarbon soluble Polyisobutylenes, grade Oppanol 150, 200 and 250 with different molecular weight of $2.5*10^6$, $4.1*10^6$ and $5.9*10^6$g/mole respectively, were acquired from BASF Company, Germany. The water soluble Xanthan Gum (XG) of molecular weight about $5.0*10^6$ g/mole was supplied from local market in Baghdad. Kerosene solvent to dissolve the Polyisobutylenes was supplied from AL–Durra Refinery. Tap water was used for dissolving of Xanthan gum polymer and for measuring its drag reduction effectiveness. The main properties of Kerosene are listed in table (3.1)(85).

Table (3.1) Properties of kerosene(85)

Properties	Kerosene
Specific gravity @15.6^{o}C	0.801
API gravity	43
Flash point ^{o}C	38
Initial boiling point ^{o}C	150
End boiling point ^{o}C	300
Aromatic content %vol	20
Aniline point ^{o}C	60
Viscosity at 25^{o}C (cst)	1.41
Color	0.5

3.2 Preparation of polymer solution

The dissolving of high molecular weight Polyisobutylene polymers were carried out in a shaking machine type KOTTERMANN 4010, Germany, 100 rpm at room temperature. This condition was used to avoid any polymer molecular degradation since the stirring device has no blade or sharp edge that could expose the polymer to high shear forces.

The method of solution preparation adopted here was to make 0.5%, 1% and 1.4% g/ml concentrations in a separate container. Thus 2.5gram, 5gram and 7gram of corresponding polymer was placed in a one liter conical flask and mixed with 500ml of the corresponding solvent. The container was placed in the electrical shaker. A homogenous solution was obtained after 3days for Oppanol B 150, 5 days for Oppanol B 200, 8 days for Oppanol B 250 and 7 days for XG. These solutions were allowed to stand at least 24 hours at room temperature prior to further investigation.

3.3 Shear degradation

The polymeric solutions of different concentrations were exposed to high speed stirred at different time. The viscosity and density of the solutions were measured as function of time and stirring speed, to evaluate the degree of polymeric degradation. The stirrer used has a sharp edge and rotating speed range 50–2000 rpm, which photo is shown in figure (3.1). Solutions of concentrations, 0.5, 1.0 and 1.4w/v percent for Polyisobutylene and Xanthan gum were exposed to such shear degradation at 1200 , 1500 and 1800 rpm stirring for different time up to 2hr for PIB and 4hr for XG. The viscosity and density for each solution were measured before starting the experiments.

Figure (3.1) Stirrer motor for shear degradation

The apparatus for shear degradation experiments consists of a 400 ml beaker, fitted with the stirrer as shown in figure (3.2). The operated procedure was carried out by placing 250 ml of corresponding polymeric solution in the beaker. The stirring device was started at a fixed rotation speed. After each time period, the stirring was stopped, and raise the container from stirring device. Samples were taken to measure the viscosity and density of the solution. After that, the stirring was continued for further time period at the fixed rotation speed. All experiments were taken place at room temperature, 30–35^{o}c.

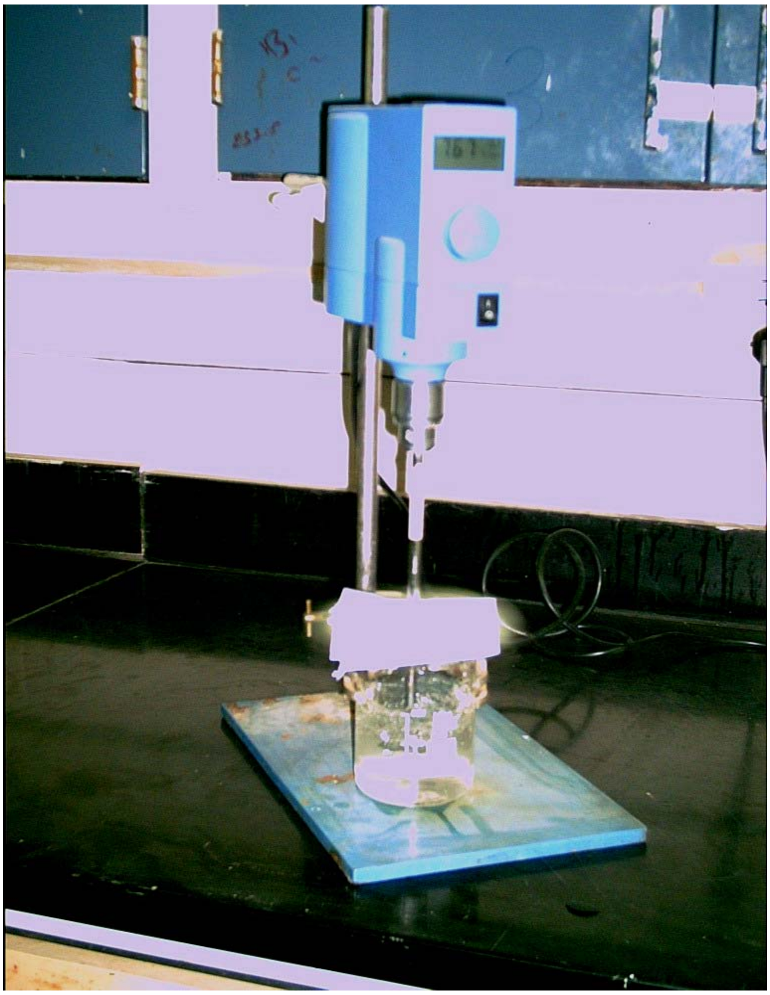


Figure (3.2) Stirrer during the work of shear degradation

3.4 Viscosity and density measurements

The viscosity was measured by using Brookfield DV–E viscometer, which measures fluid viscosity at a given shear rate. The principle of operation of the DV–E viscometer is to rotate a spindle, which is immersed in the test fluid until the fluid is at the immersion groove on the spindles shaft through calibrated spring. The viscous drag of fluid against the spindle is measured by the spindle deflection. The viscosity measurements of DV–E viscometer is in centipoises or milli Pascal seconds. The viscometer was set in either speed select or spindle select mode. When set in the left position, the operator may select speed of rotation. When set in the right position the operator may select spindle. The viscometer DV–E is shown in figure (3.3). DV–E viscometers are provided with a set of four spindle. Each spindle must have entry code number to calculate viscosity value. The viscometer memory contains parameters for all spindle and the digit entry code for each spindle are listed in table (3.2).

Table (3.2) Code of spindles for DV–E viscometer

Spindle	LV_1	LV_2	LV_3	LV_4
Code	61	62	63	64

There are 18 rotational speed available on DV–E viscometer, those are 0.3, 0.5, 0.6, 1, 1.5, 2, 2.5, 3, 4, 5, 6, 10, 12, 20, 30, 50, 60 and 100rpm.

The density of polymeric solution before and after the degradation experiments was measured by using pyknometer size 50cm^3. The sample weights were measured by a sensitive digital balance type (METTLER, AE 163, GERMANY) to the range of 0.1 mg.

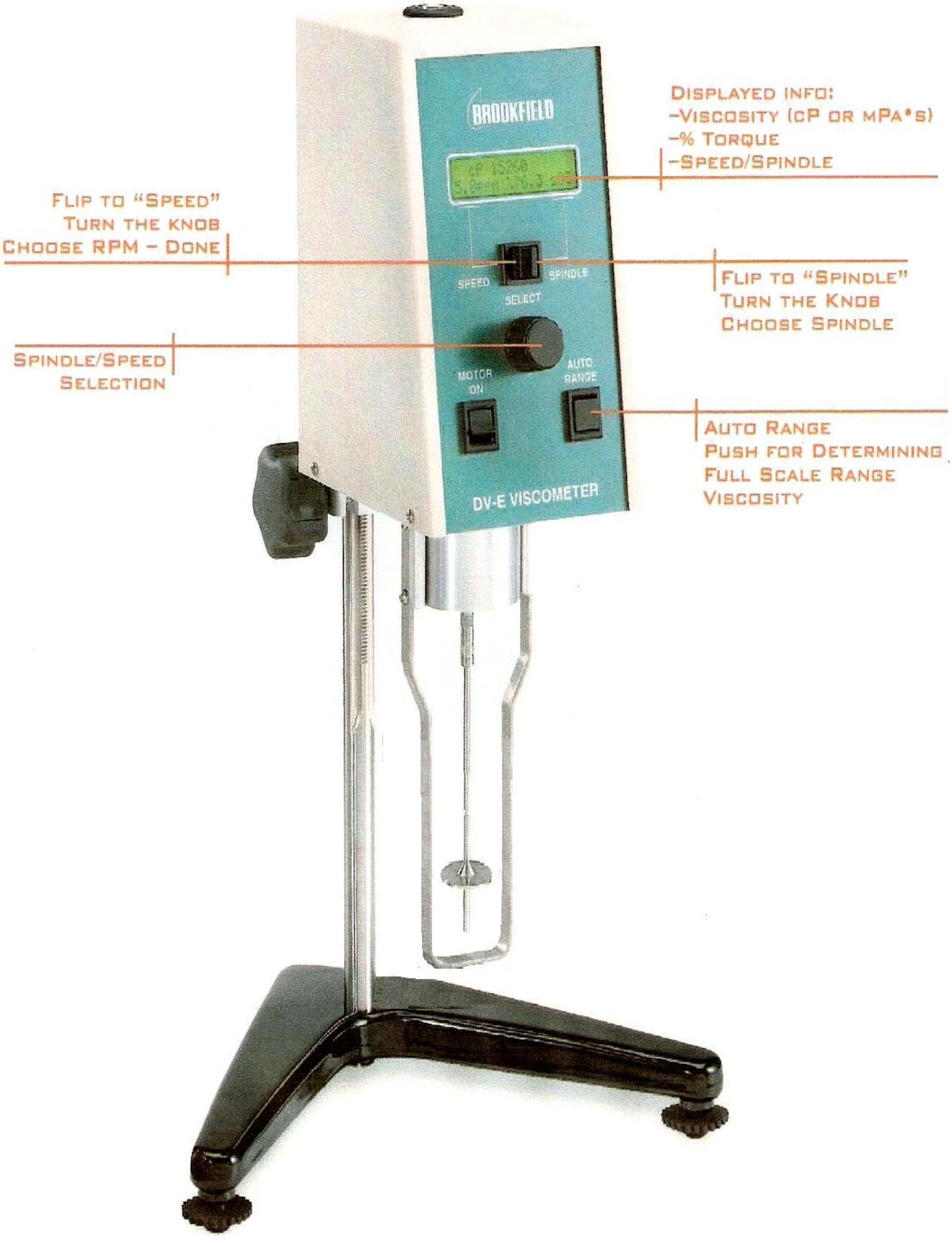


Figure (3.3) DV-E viscometer

3.5 Drag reduction measurements

3.5.1 Flow loop

The performance of the drag reducing additives was evaluated in a laboratory scale circulation loop(24). The schematic diagram of experimental set up is shown in figure (3.4).

The fluid container of about $0.49 m^3$ capacity was fitted with a positive displacement gear pump of 50.8mm diameter and 1440rpm. This type of pump was used to avoid polymer mechanical degradation which reduces usually the drag reducing efficiency. Pipe of 0.03175m inside diameter was used to perform the flow measurement. The test section was 2m long and located away from the entrance to get the fully developed region. The fluid flow was controlled by means of ball valves, while pressure drop in the test section was measured by U–tube manometer filled with water. Float flow meter of 50.8mm and flow indication range ($0.6–6 m^3/hr$) was used to measure the solution flow rates. The calibration curve of the flow meter is shown in figure (3.5).

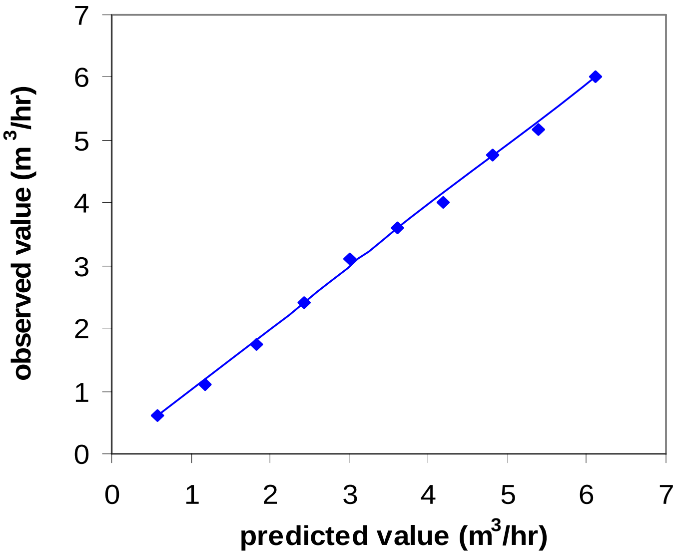


Figure (3.5) Calibration of flow meter for water

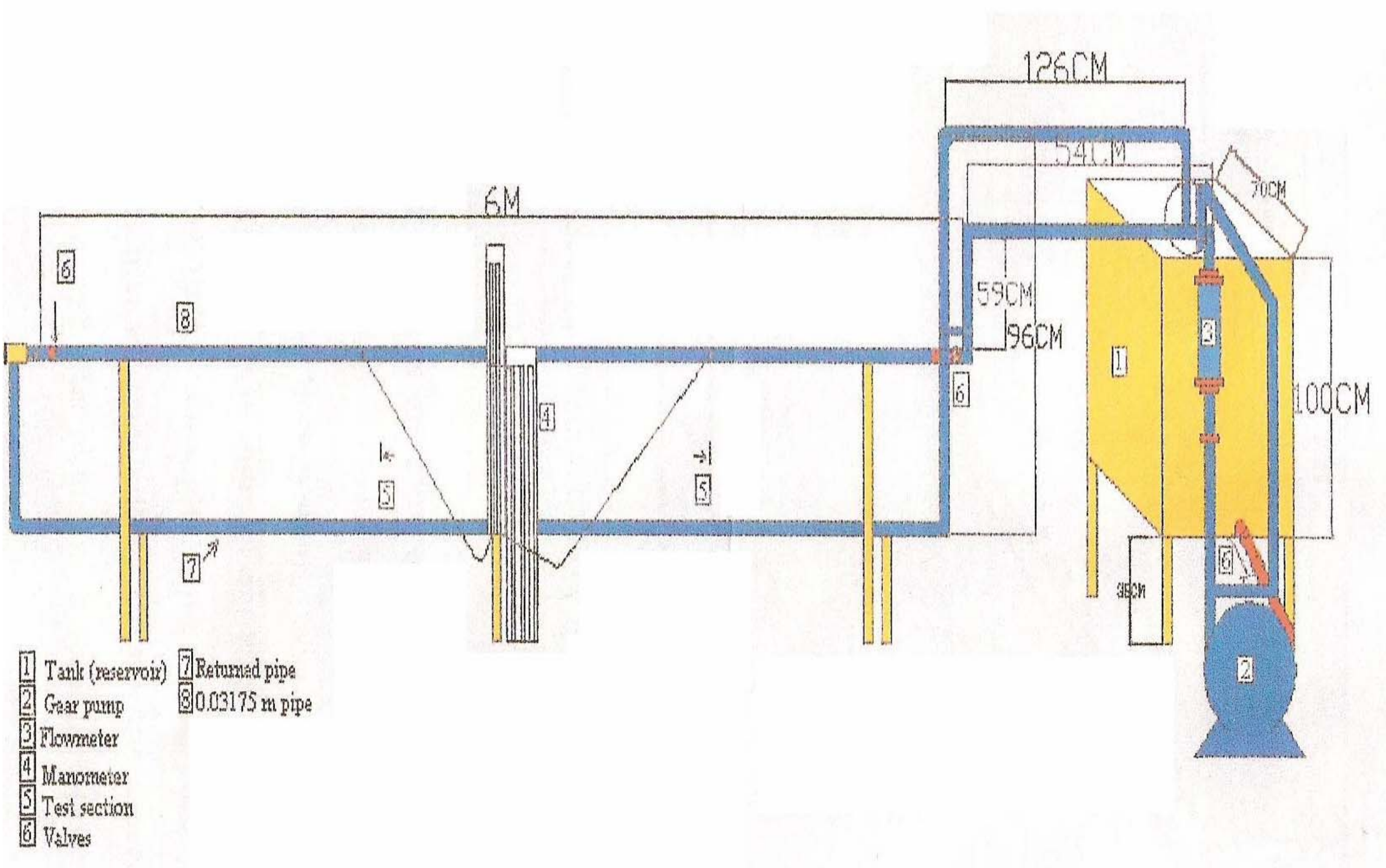


Figure (3.4) Schematic diagram for the

Circulation- loop system

3.5.2 Experimental procedure

The following steps were performed in each drag reduction experiments.

1. The container was filled with 160 litter of tap water.
2. To avoid any error in manometers readings, bubbles were allowed to flow away by controlling the pressure tapings.
3. The external gear pump was operated.
4. The required amount of concentrated amount of Xanthan gum was mixed with 500ml tap water. The prepared solution was then added carefully to the container.
5. After 30 minute circulation, the reading of the manometers was recorded.
6. These steps were repeated upon change in concentration and flow rate.
7. For degradation experiments purpose the manometers reading was taken every 1 hour flow.

3.6 Calculations

The percentage viscosity reduction %RV was calculated using the solution viscosity before and after degradation as follows:

$$\%RV = \frac{\mu_b - \mu_a}{\mu_b} * 100 \qquad \ldots(3.1)$$

Where

μ_b= viscosity of solution before degradation

μ_a = viscosity of solution after degradation

Reynolds number (Re) was calculated using the solution volumetric flow rate readings (Q) , density (ρ) , viscosity (μ) and pipe diameter (d) for each run as follows:

$$\mathrm{Re} = \frac{\rho\ u\ d}{\mu} \qquad \ldots(3.2)$$

Where

u =Q/A

and A=area = $(\pi/4)d^2 \times 3600$

The corresponding calculated Re values are listed in table (3.3)

Table (3.3) Calculation of Reynolds number

Q (m^3/hr)	u (m/s)	Re
6	2.1	66675
5.2	1.8	57150
4.4	1.5	47625
3.6	1.26	40005
2.8	0.98	31115
2	0.7	22225

Pressure drop readings through testing sections before and after drag reducer addition , were needed to calculate the percentage drag reduction %DR as follows(13):

$$\%DR = \frac{\Delta P_{untreated} - \Delta P_{treated}}{\Delta P_{untreated}} * 100 \qquad \ldots(3.3)$$

Where

$\Delta P_{untreated}$ is the pressure drop in the pipeline with no drag reducer present and $\Delta P_{treated}$ is the pressure drop in the pipeline with drag reducer present. equation (3.3) assumes the flow rate is constant.

Chapter Four

Results and Discussion

4.1 Scope of the Investigation

Dilute solutions of Oppanol polymers in kerosene were prepared in concentrations of 0.5, 1.0 and 1.4w/v %.We use this concentration because it was not easy to prepare the polymeric solutions in higher concentrations than 1.4w/v %, due to difficulties in dissolving and to high viscosity of such solutions and the concentrations below 0.5% leads to no degradation occur. The solutions of Xanthan gum were in concentration of 0.5 and 1.0 w/v %. The viscosity and density of original solutions are listed in table (4.1).

Table (4.1) Viscosity and density of polymeric solutions

Polymer	Mw (million) g/mole	Concentration % g/ml	μ (cp)	ρ (g/ml)
Oppanol 150	2.5	0.5	11.82	0.791
		1.0	44.8	0.794
		1.4	120	0.798
Oppanol 200	4.1	0.5	16.44	0.793
		1.0	83.1	0.796
		1.4	231.9	0.802
Oppanol 250	5.9	0.5	63.2	0.798
		1.0	293	0.804
		1.4	623	0.808
Xanthan Gum	5.0	0.5	54.9	1.0102
		1.0	276.2	1.0117

These solutions exposed to shear degradation of mechanical stirrer with blades to indicate the change that took place on polymer chains as a result of mechanical force that was applied to it. The effects of concentrations, stirring speeds, molecular weights and exposure time on any changes in the viscosity and density of polymeric solution were studied. The relation between the decrease in drag reduction effectiveness with flowing time in laboratory turbulent flow loop and polymers degradation were also studied. Mechanical degradation refers to the chemical process in which the activation energy of polymer chain scission is exceeded by the mechanical action on the polymer chain, and bond rupture occurs.

4.2 Mechanical degradation of Oppanol

4.2.1 Viscosity changes

4.2.1.1 Stirring speed effect

Polyisobutylene solutions are non–Newtonian fluid and as thixotropic liquids(37)there viscosity are changed with high speed stirring and the solution become thinner and less viscous(86).

The viscosity changes of Polyisobutylene (Oppanol) polymers dissolved in kerosene were investigated during stirring by a mechanical stirrer. The results of the three different concentrations, 0.5, 1.0 and 1.4 after 2hr exposure time are illustrated in figures (4.1), (4.2) and (4.3) for oppanol 150, 200 and 250 respectively. These figures show the lowering of viscosity as the stirring speed increases for all three concentrations. While the sensitivity of viscosity with speed variations depends on the polymer concentration and hence on the solution viscosity. Thus the high viscous solution as in concentration of 1.4%w/v for all oppanol type are affected more by speed increase. Furthermore, the viscosity changes are more affected by molecular weight of Oppanol polymers. Those Oppanol 250 is more susceptible to shear degradation and therefore the viscosity of its solution decreases more and gradually with exposure time. Thus after 2hr stirring at 1800rpm the viscosity of 1.4% solution of Oppanol B 250 drops from 623 cp of original value to about 205.3cp .The corresponding values for oppanol 150 are 120cp original drops to about 81.7cp after stirring.

Moreover table (4.2) summarized selected results to clarify the effect of stirring speed on viscosity lowering of 1.4% w/v solutions of the three types of Oppanol polymers at 2hr exposure time. These results indicate clearly the effect of high level of shearing on viscosity reduction due to mechanical shear degradation of polymer molecules. Shearing at lower stirring speed (rpm lower than 1200) resulted in low viscosity reduction of polymeric solutions.

Table (4.2) Effect of stirring speed on the viscosity of Oppanol Solutions at 1.4% w/v, 2hr stirring time

rpm	B-150	B-200	B-250
_	120	231.9	623
1200	102.6	159.9	368.4
1500	89.1	133.7	317.1
1800	81.7	100.8	205.3

The decrease in the polymer solution viscosity with increasing time of shearing is shown in figures (4.4) through (4.12). In figure (4.4) the viscosity of Oppanol 150 0.5% solution is dropped from 11.82cp before exposure to shear degradation to 10.8cp after 2hr of shearing at 1200rpm and to about 10.03cp at 1500rpm and 9.61cp at 1800rpm both at 2hr stirring. Figure (4.5) shows that the viscosity of 1.0% Oppanol 150 solution is dropped from 44.8cp before stirring to 34.3cp at 1200 rpm, 33.4cp at 1500 rpm and 31.9cp at 1800 rpm all at time 2hr exposure time. Figure (4.6) shows the results for Oppanol 150 at concentration 1.4% indicating that the viscosity dropped from 120cp to 102.6cp, 89.1cp and 81.7cp for 1200, 1500 and 1800 rpm respectively after 2hr shearing. The same relationship is shown in figures (4.7) to (4.9) for Oppanol 200 and figures (4.10) to (4.12) for Oppanol 250 solutions. From these figures could be concluded that the scission or degradation of polymer chains may take place as a result of high shear rates. The degradation increases as speed increases and as time of shearing increases also.

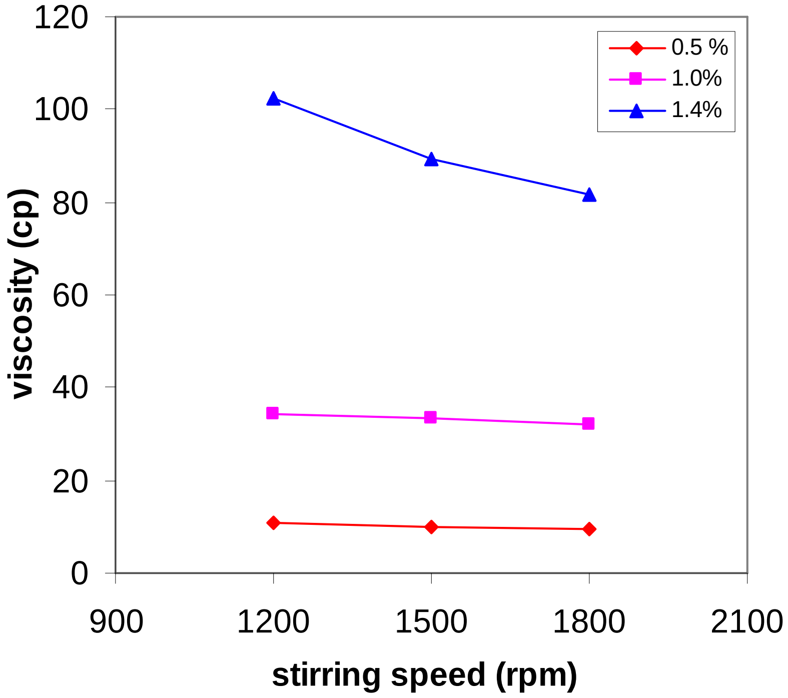


Figure (4.1) Effect of stirring speed on the viscosity of Oppanol B-150 at 2hr exposure time

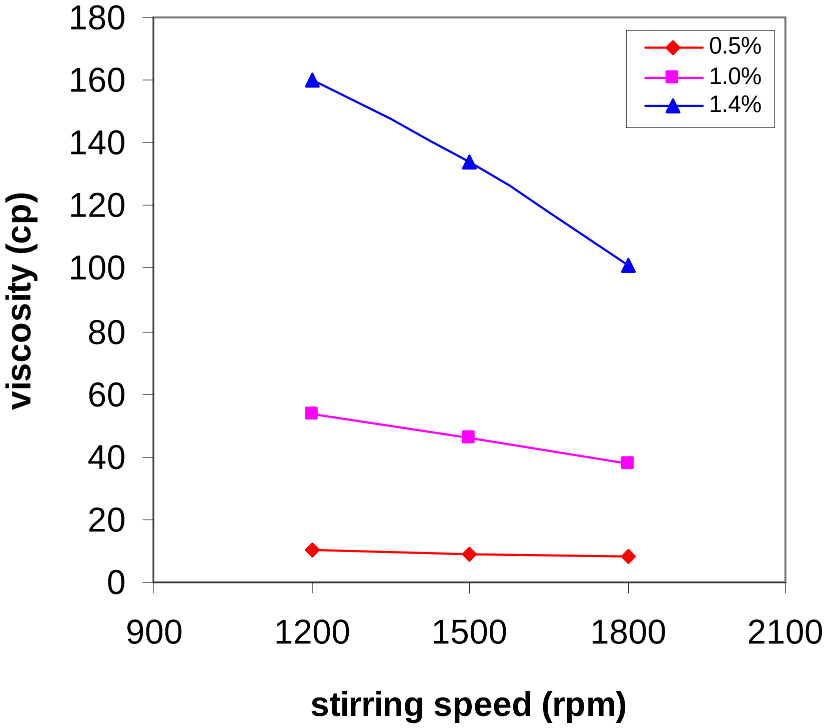


Figure (4.2) Effect of stirring speed on the viscosity of Oppanol B-200 at 2hr exposure time

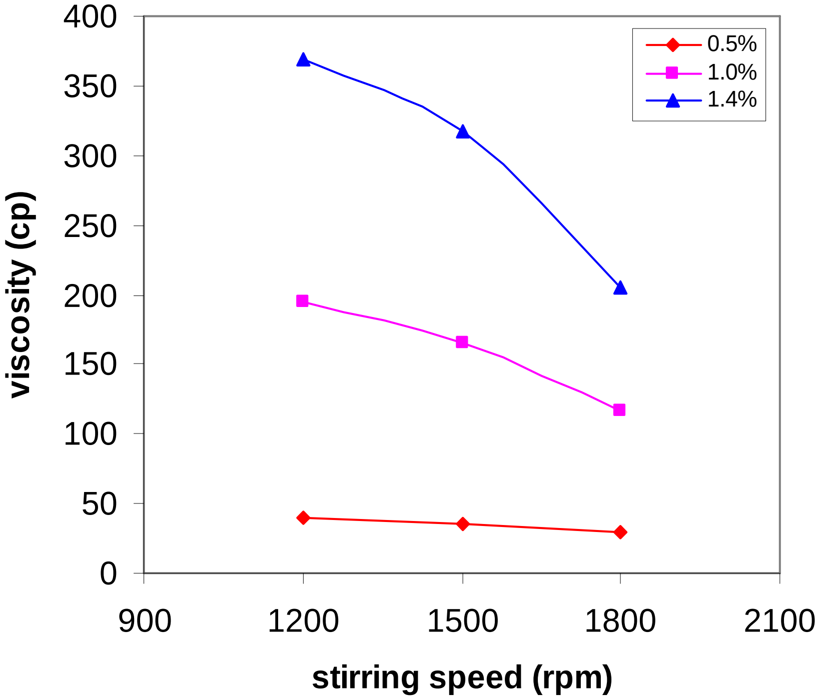


Figure (4.3) Effect of stirring speed on the viscosity of Oppanol B-250 at 2hr exposure time

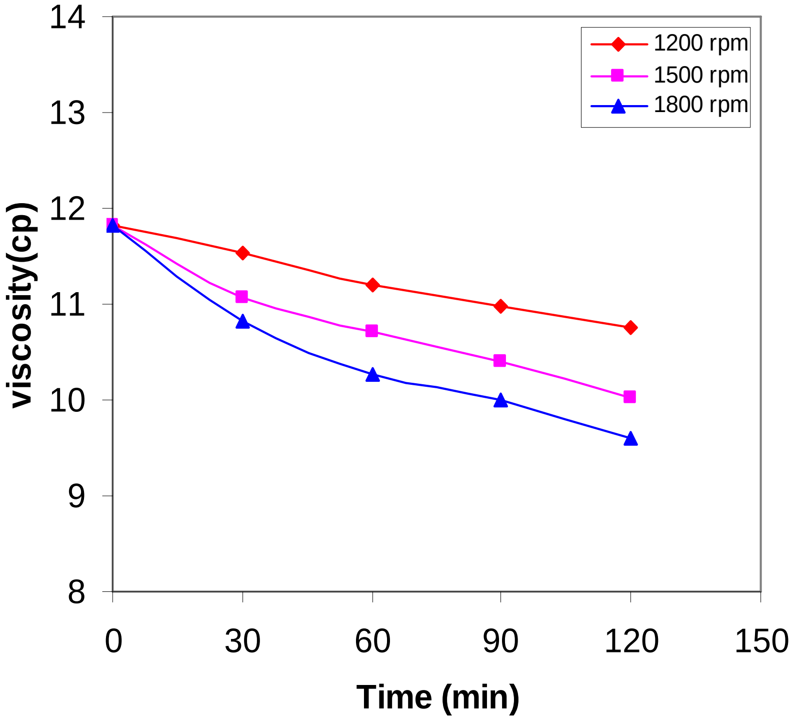


Figure (4.4) Effect of exposure time on the viscosity of 0.5w/v % Oppanol B-150 solution

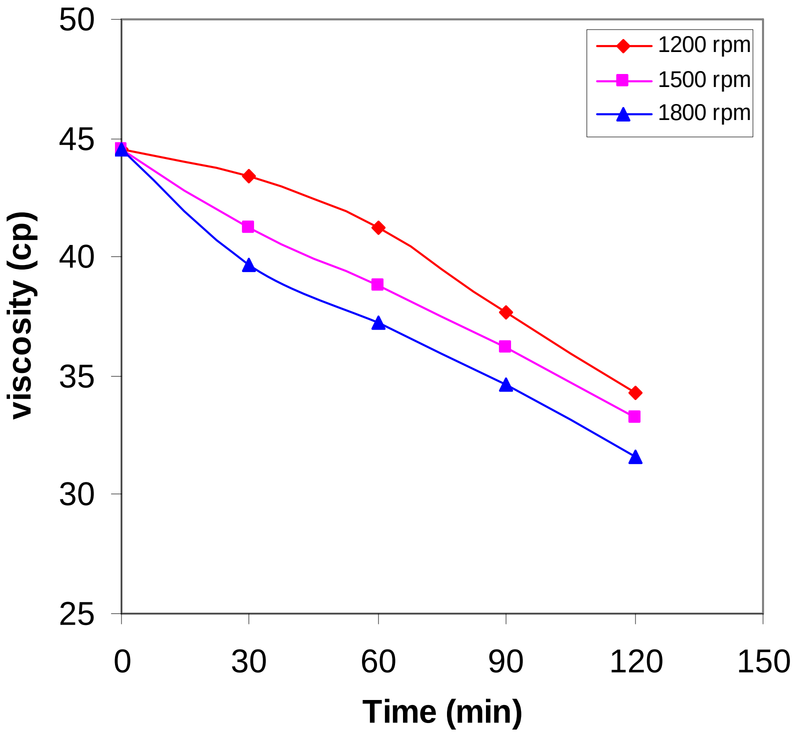


Figure (4.5) Effect of exposure time on the viscosity of 1.0 w/v % Oppanol B-150 solution

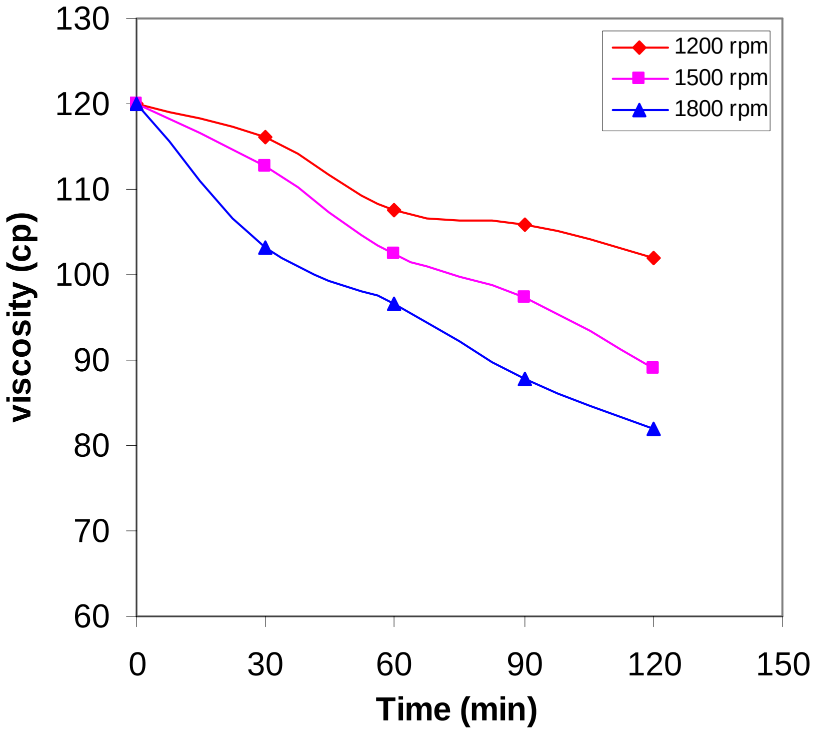


Figure (4.6) Effect of exposure time on the viscosity of 1.4w/v % Oppanol B-150 solution

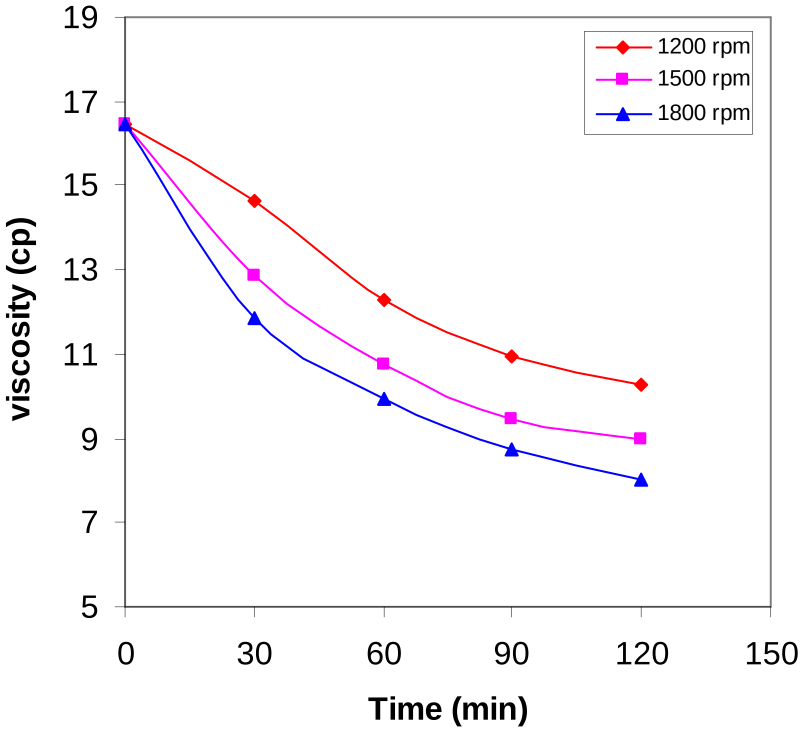


Figure (4.7) Effect of exposure time on the viscosity of 0.5w/v % Oppanol B-200 solution

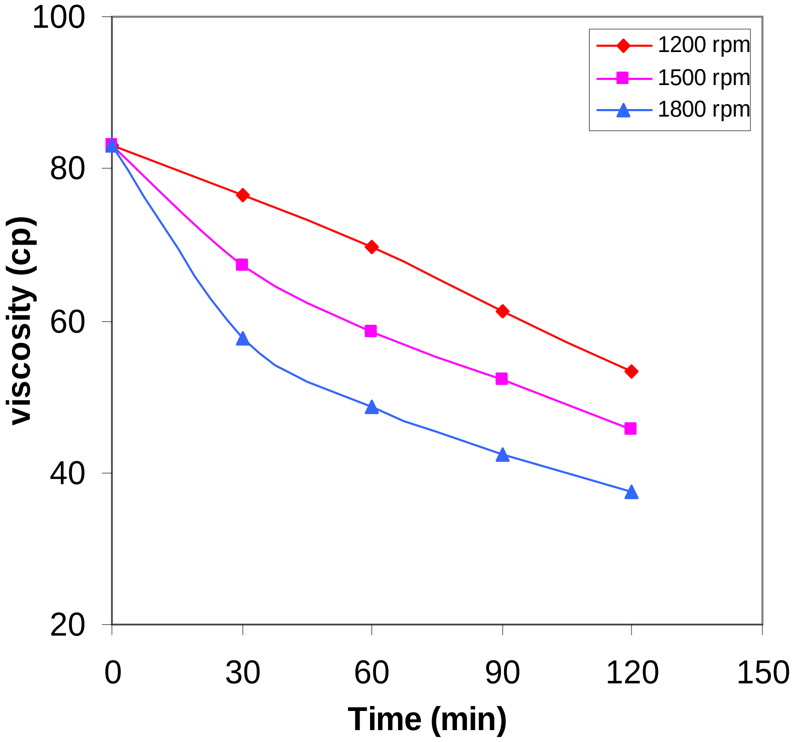


Figure (4.8) Effect of exposure time on the viscosity of 1.0 w/v % Oppanol B-200 solution

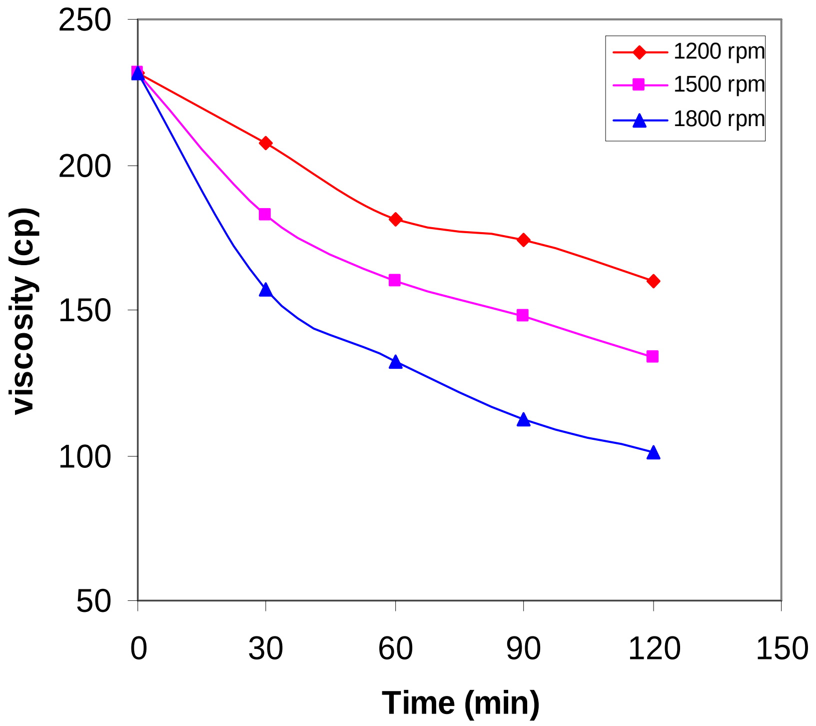


Figure (4.9) Effect of exposure time on the viscosity of 1.4w/v % Oppanol B-200 solution

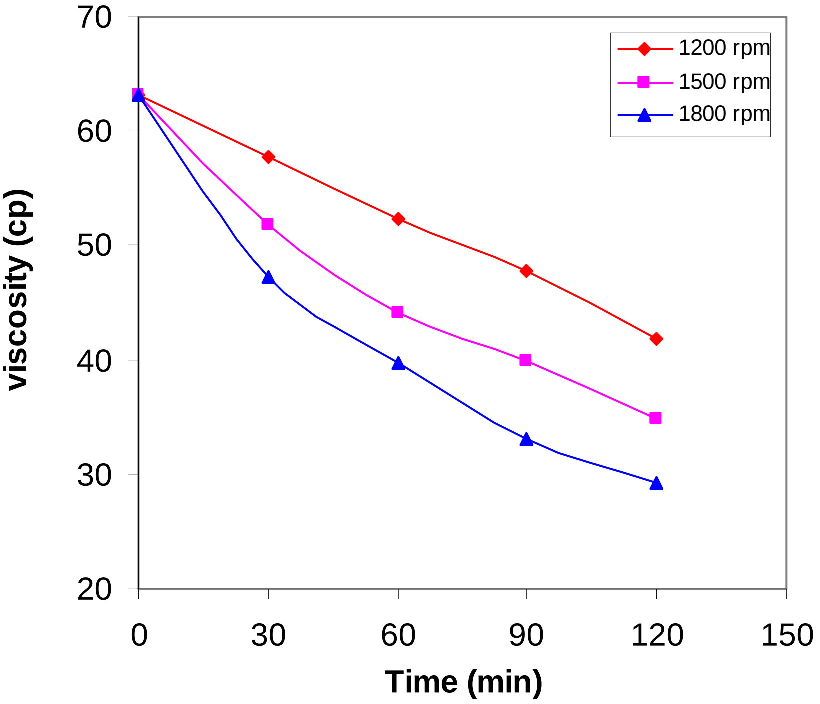


Figure (4.10) Effect of exposure time on the viscosity of 0.5w/v % Oppanol B-250 solution

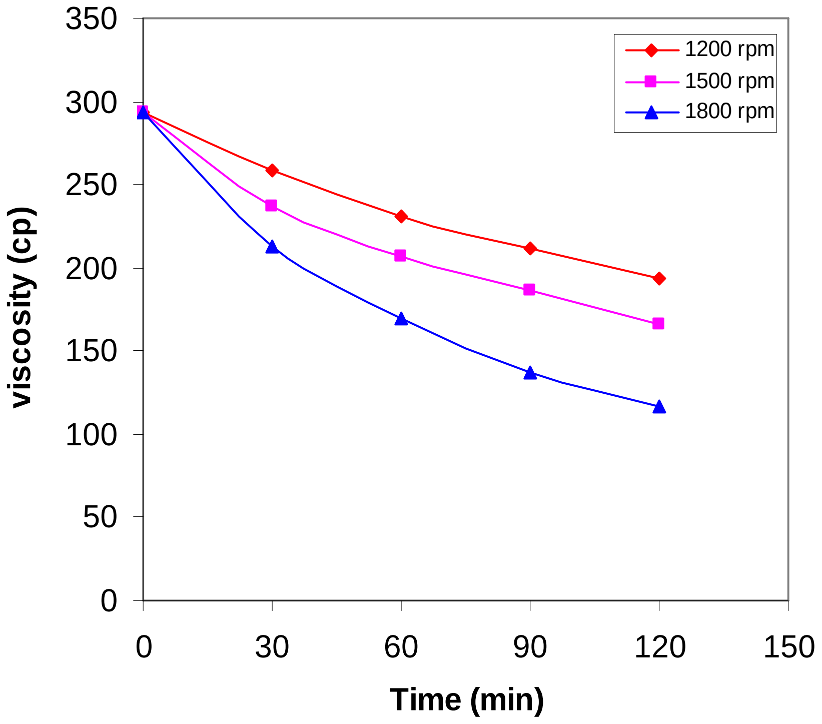


Figure (4.11) Effect of exposure time on the viscosity of 1.0w/v % Oppanol B-250 solution

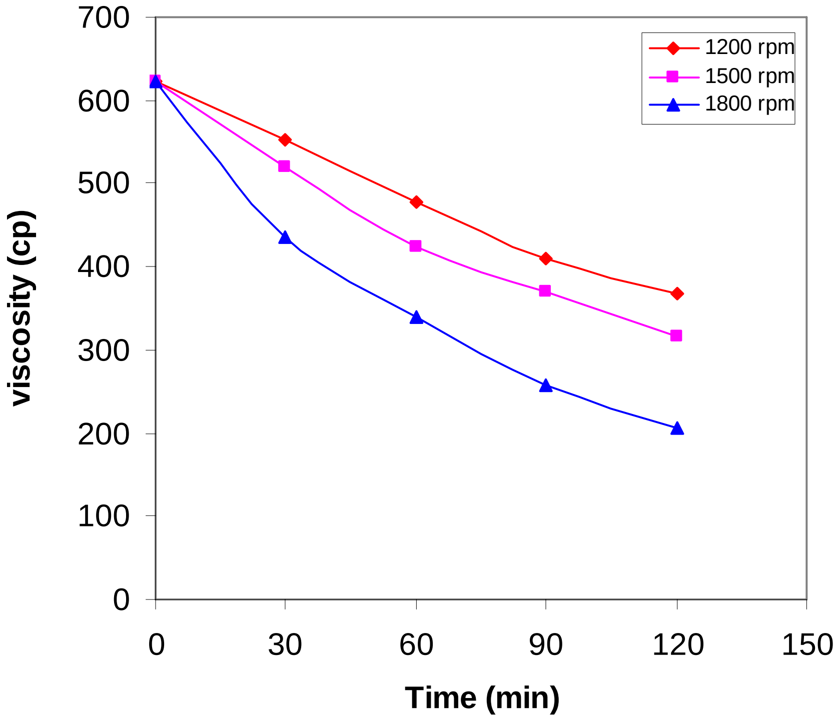


Figure (4.12) Effect of exposure time on the viscosity of 1.4w/v % Oppanol B-250 solution

It is worthy to discuss the time dependence of molecular shear degradation in terms of percentage change of the viscosity, as illustrated in figures (4.13) through (4.21) for the three Oppanol types at different concentrations. Thus indicate that the percentage decrease in the viscosity solutions increase gradually with increasing the exposure time. Furthermore, the effect of time on the viscosity reduction is lower for Oppanol 150 than that for Oppanol 200 and 250. Therefore, the results for shear degradation for 1.0% polymeric solution for the three polymers at 1800rpm shearing could be taken to compare the time effect as shown in figures (4.14), (4.17) and (4.20). The solution viscosity drops from 11.4% after 30min to about 28.7% reduction after 120min stirring for Oppanol 150. While, the corresponding values for Oppanol 200 and 250 are 30.4% to 54.7% and 27.2% to 60.3% reduction respectively. Those indicating that the viscosity of the high molecular weight type solutions is more sensitive to shear degradation.

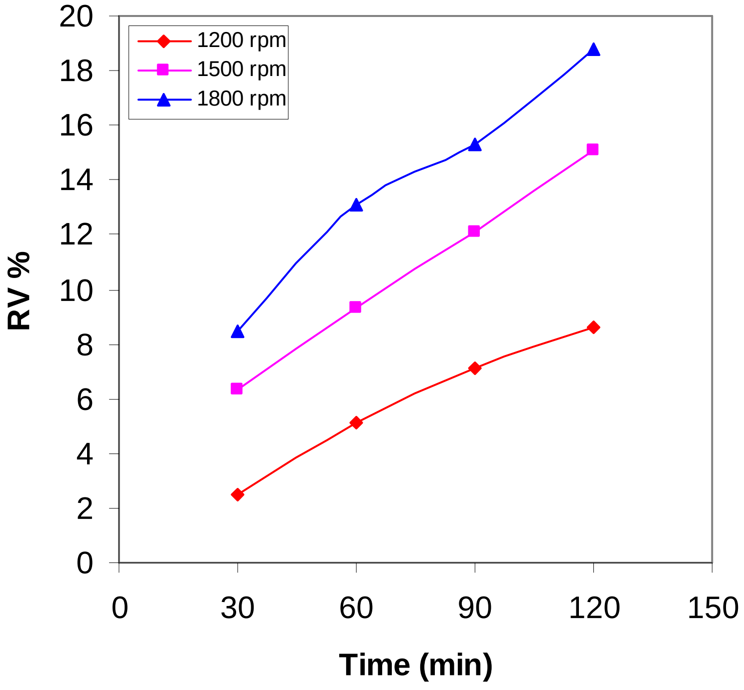


Figure (4.13) Percentage viscosity reduction vs. time by shearing of 0.5 % Oppanol B-150 solution

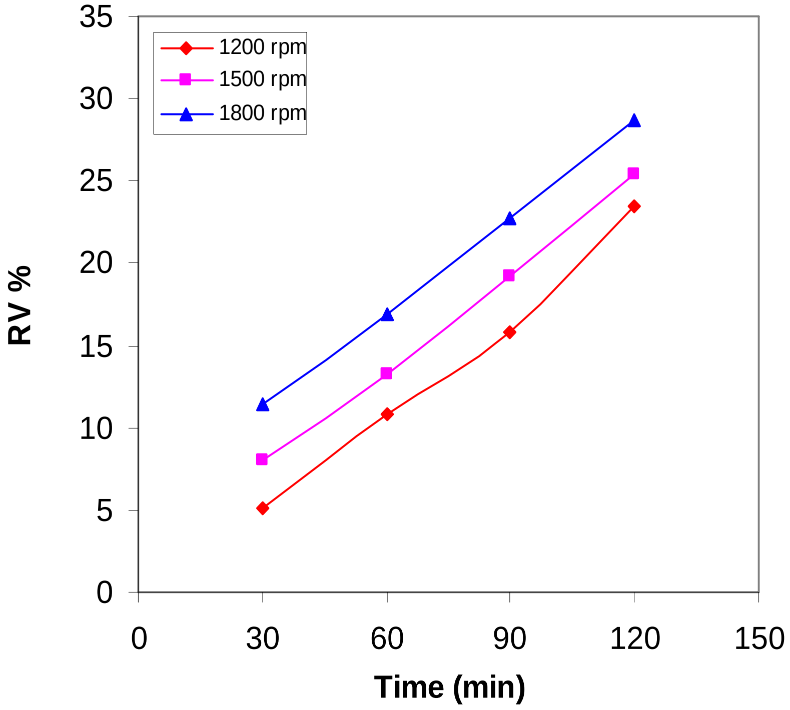


Figure (4.14) Percentage viscosity reduction vs. time by shearing of 1.0 % Oppanol B-150 solution

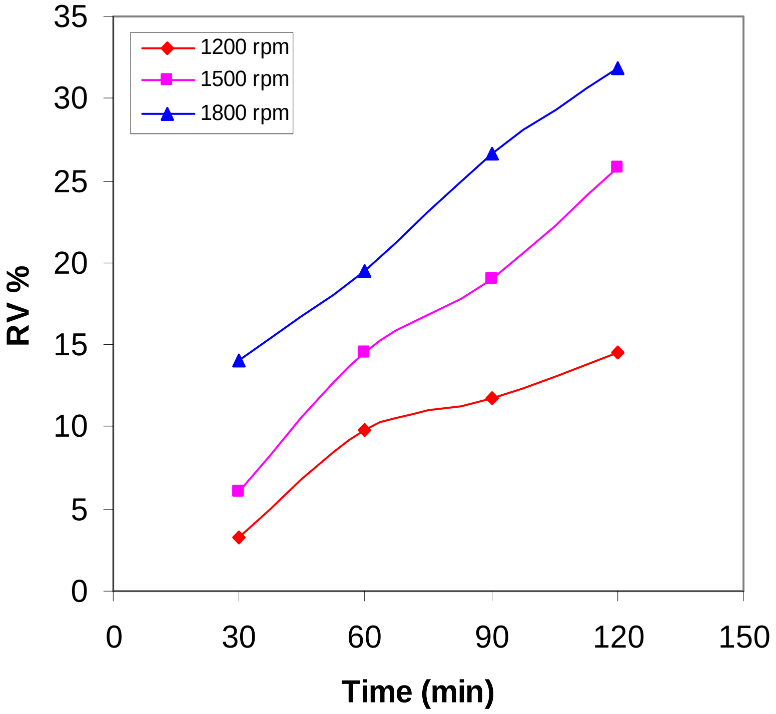


Figure (4.15) Percentage viscosity reduction vs. time by shearing of 1.4 % Oppanol B-150 solution

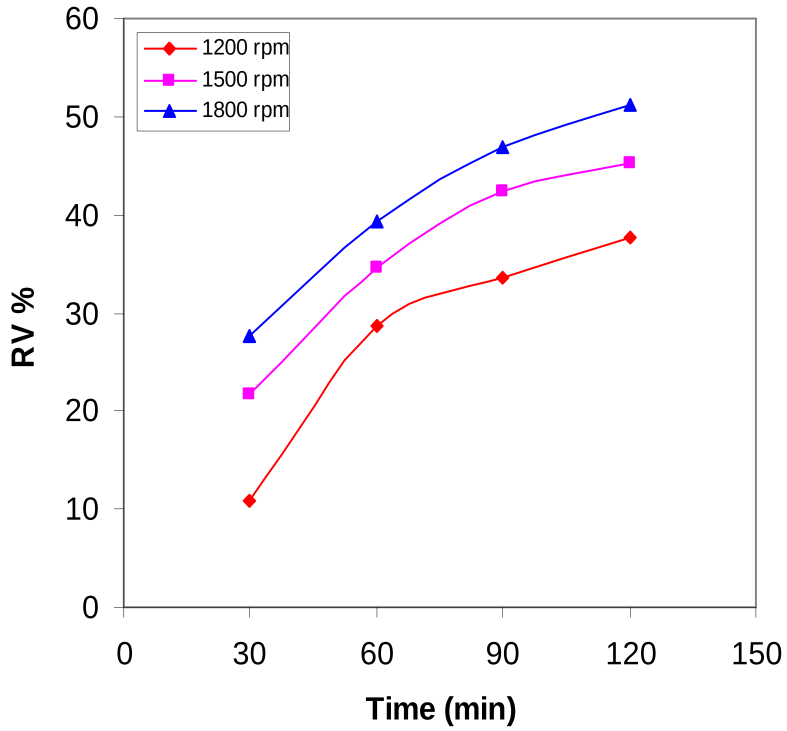


Figure (4.16) Percentage viscosity reduction vs. time by shearing of 0.5 % Oppanol B-200 solution

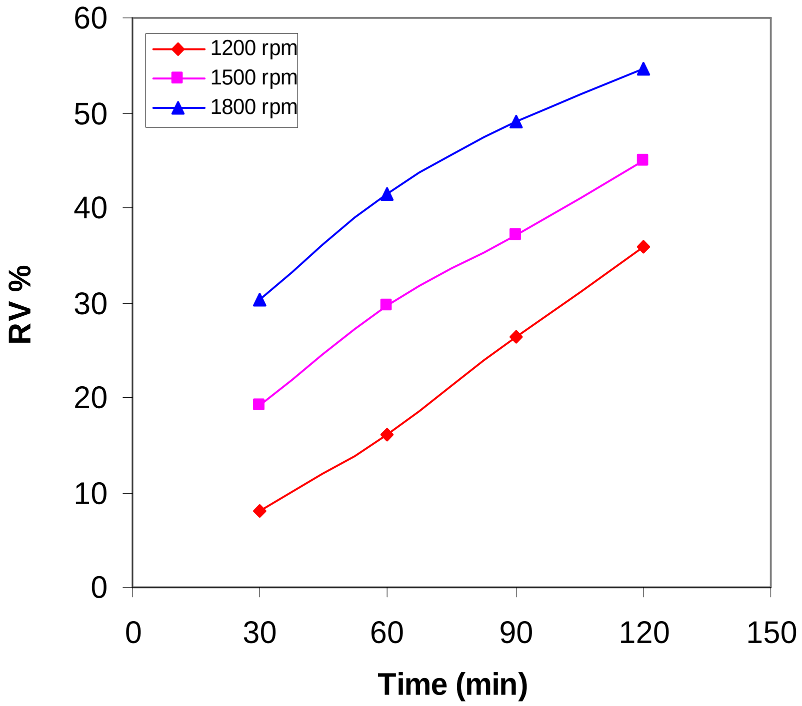


Figure (4.17) Percentage viscosity reduction vs. time by shearing of 1.0 % Oppanol B-200 solution

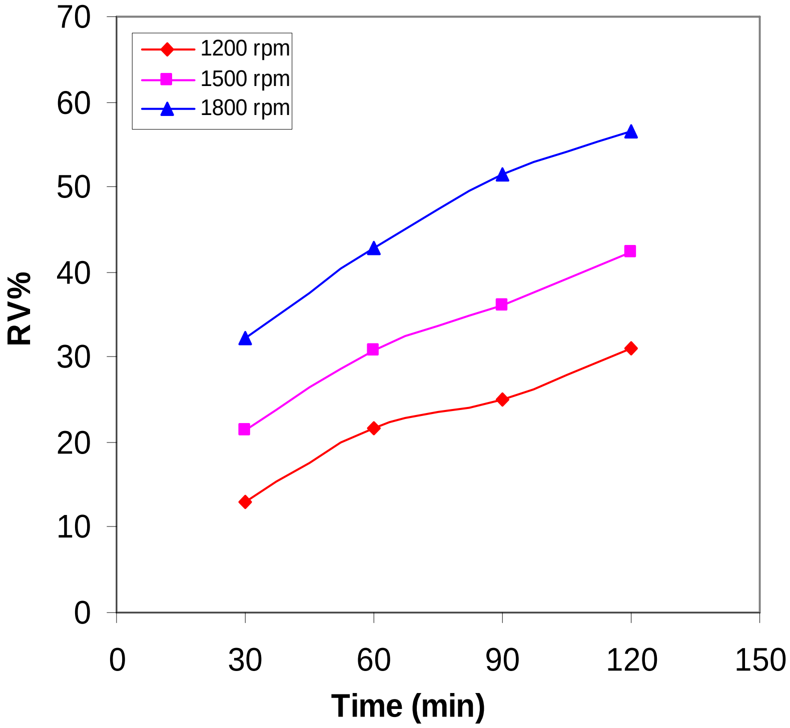


Figure (4.18) Percentage viscosity reduction vs. time by shearing of 1.4 % Oppanol B-200 solution

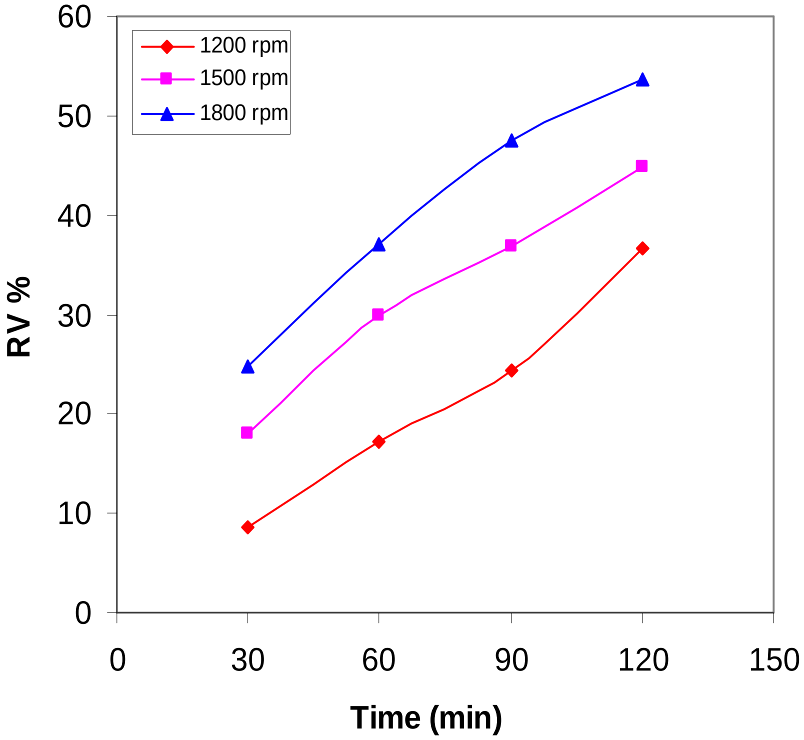


Figure (4.19) Percentage viscosity reduction vs. time by shearing of 0.5 % Oppanol B-250 solution

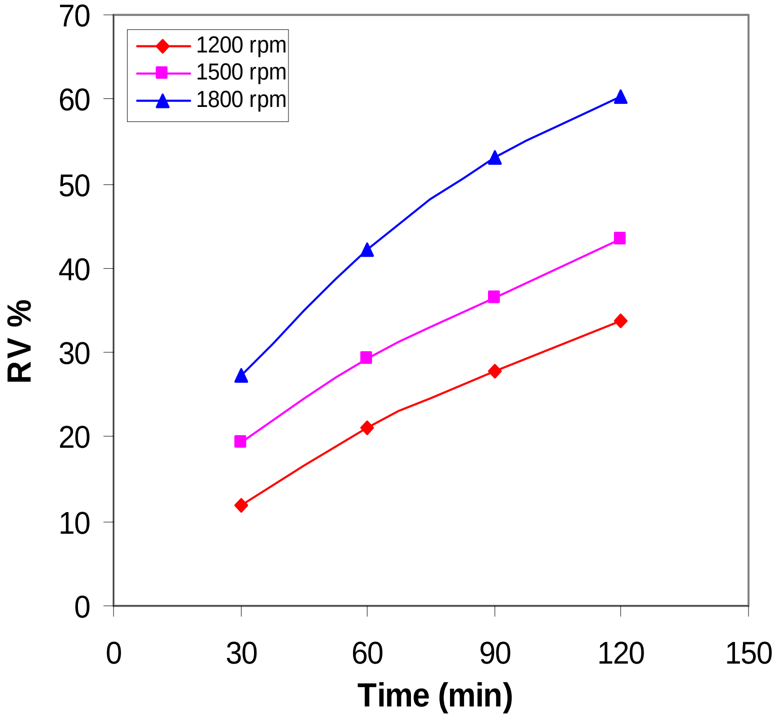


Figure (4.20) Percentage viscosity reduction vs. time by shearing of 1.0 % Oppanol B-250 solution

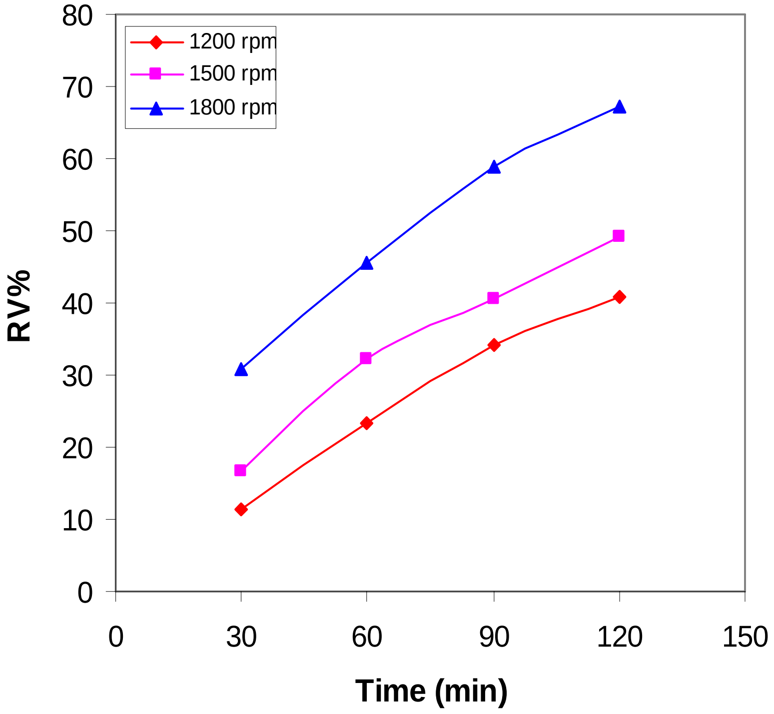


Figure (4.21) Percentage viscosity reduction vs. time by shearing of 1.4 % Oppanol B-250 solution

4.2.1.2 Concentration effect

The effect of concentration of polymer solutions on the scission of polymer chains by high speed stirring had been investigated by change of viscosities, as shown in figures (4.22) to (4.24). The results indicate that viscosity of polymeric solutions increase dramatically with the increase in the concentration. Three polymer concentrations were chosen, namely 0.5%, 1.0% and 1.4%w/v to evaluate the concentration dependence of shear degradation of the three Oppanol polymers by expose there solutions to high speed stirring. It was found that the low concentration solutions are less sensitive to shear degradation by mechanical stirring. The polymer chain scission is largely dependent on the concentration of polymer solution that lead to the conclusion that the polymer chains were not broken by contact only with solvent but even though by contact of a polymer chain (entanglement) with other chains(60).

Figure (4.23) shows that the viscosity of 1.4%w/v concentration of Oppanol 200 solution decreases rapidly during the first 30min stirring while as the concentrations decreased the susceptibility to degradation was decreased also. The viscosity of 1.4%w/v solution decline from 231.9cp before stirring to 157.1cp at 30min exposure, and reaches about 100.8cp value after 120min stirring. While for concentration 1.0%w/v viscosity change from initial value of 83.1cp to 37.6cp at 2hr stirring. The corresponding values for the 0.5%w/v solutions are about 16.44cp initially to about 8.04cp at 2hr stirring.

Figure (4.24) indicates that the viscosity show sharp decrease during the first hour for 1.4% of Oppanol 250 solutions. It was changed from 623cp initially to about 434.9cp after 30min shearing at 1800 rpm, and was decreased to about 339.1cp after 60min and about 205.3cp after 120min shearing.

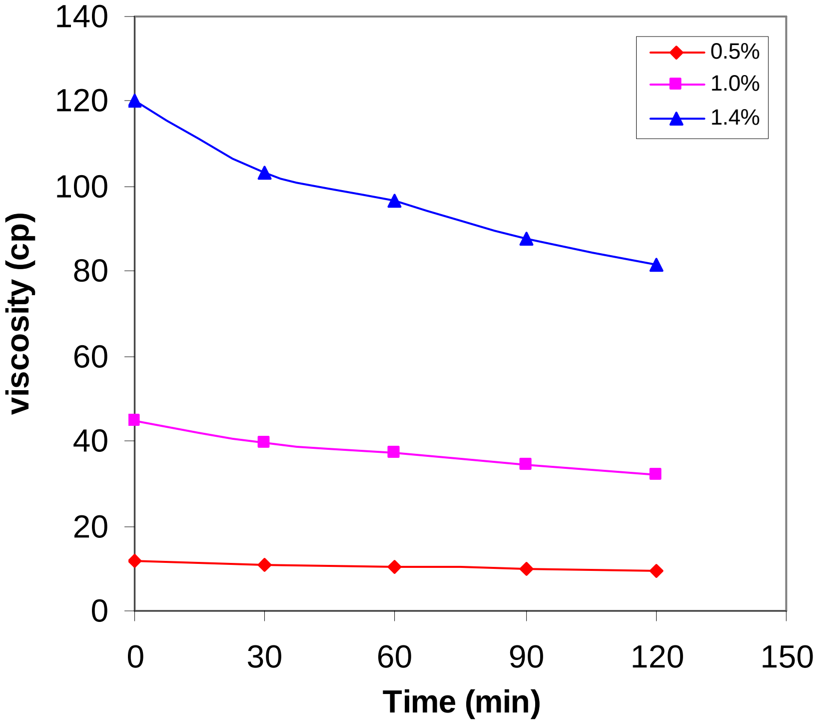


Figure (4.22) Concentration effect on viscosity for Oppanol B-150 solution at 1800 rpm

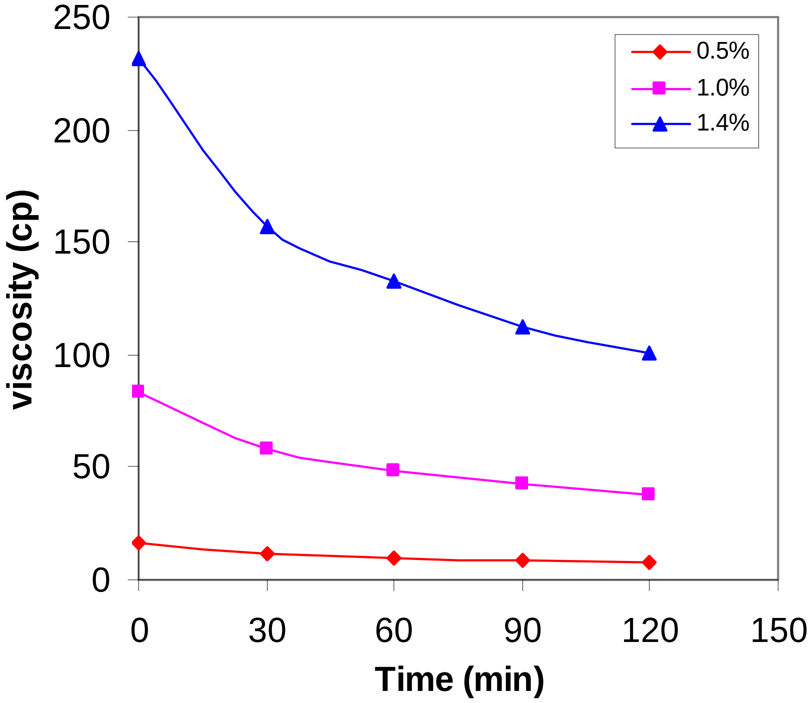


Figure (4.23) Concentration effect on viscosity for Oppanol B-200 solution at 1800 rpm

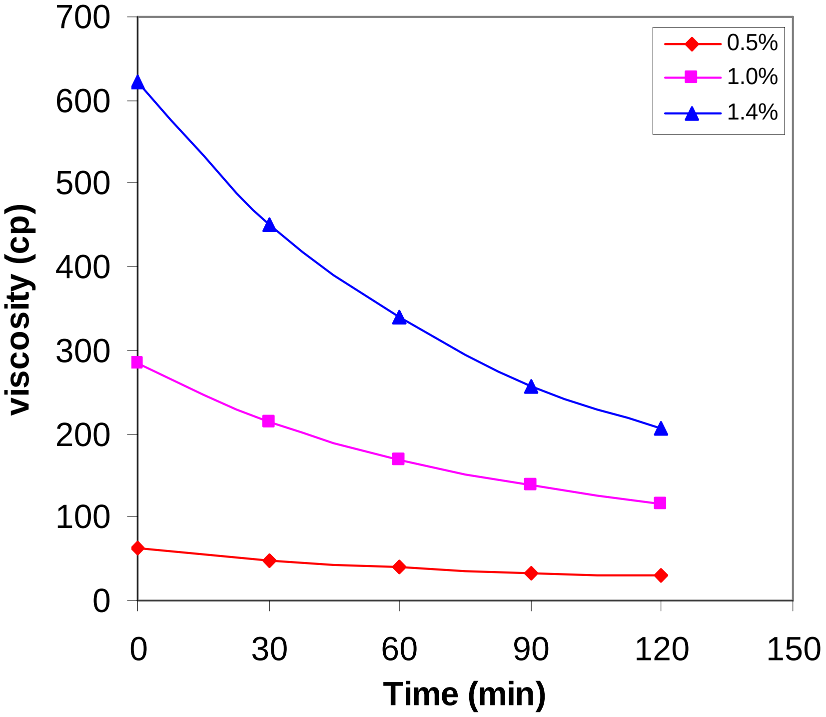


Figure (4.24) Concentration effect on viscosity for Oppanol B-250 solution at 1800 rpm

It was worthy to show the effect of stirring at 1800rpm on percentage decrease of the viscosities of polymeric solutions at different concentrations and stirring time, as illustrated in figures (4.25) through (4.27). The viscosity reduction for Oppanol 150 of concentrations 0.5, 1.0 and 1.4%w/v at 2hr stirring at 1800rpm were 18.8, 28.7 and 31.9% respectively, as shown in figure (4.25). The corresponding data for Oppanol 200 at the same conditions were 51.1, 54.7 and 56.5% for the three concentrations respectively as shown in figure (4.26). While for Oppanol 250 were 53.6, 60.3 and 67.1% respectively of viscosity reduction, as shown in figure (4.27).

All above results indicate clearly, that the mechanical degradation increases as the polymeric concentration increases, leading to more viscosity lowering. Furthermore the exposure time has a predominant effect on polymeric degradation indicated by percent reduction of the solution viscosity. The time effect could be seen clearly in figure (4.27) for Oppanol 250 as an example. The viscosity was reduced in the order 30.7, 45.6 and 67.1% at stirring time 0.5, 1.0 and 2hr respectively for 1.4% solution concentration.

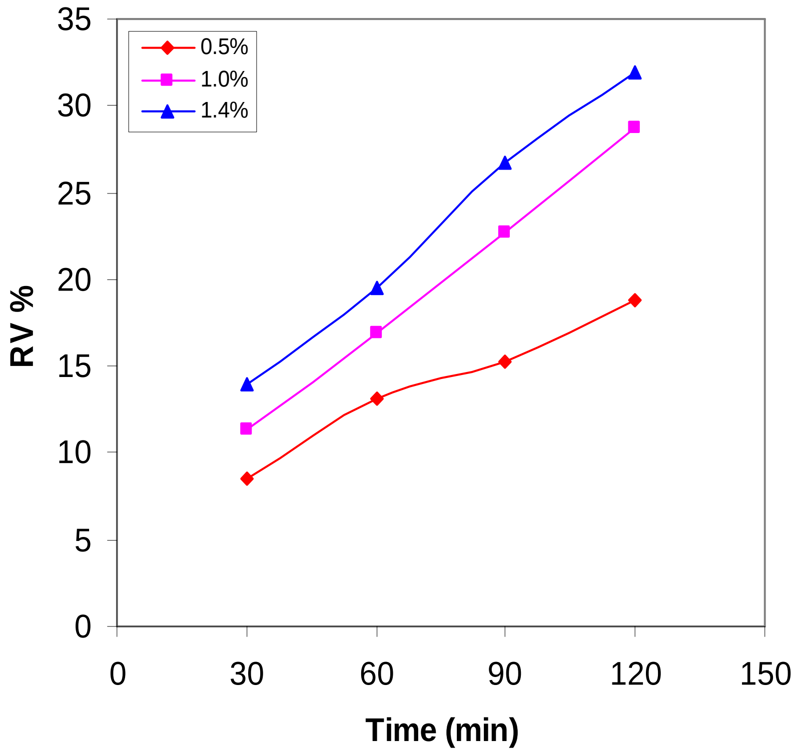


Figure (4.25) Percentage viscosity reduction vs. time for Oppanol B-150 solution at 1800 rpm

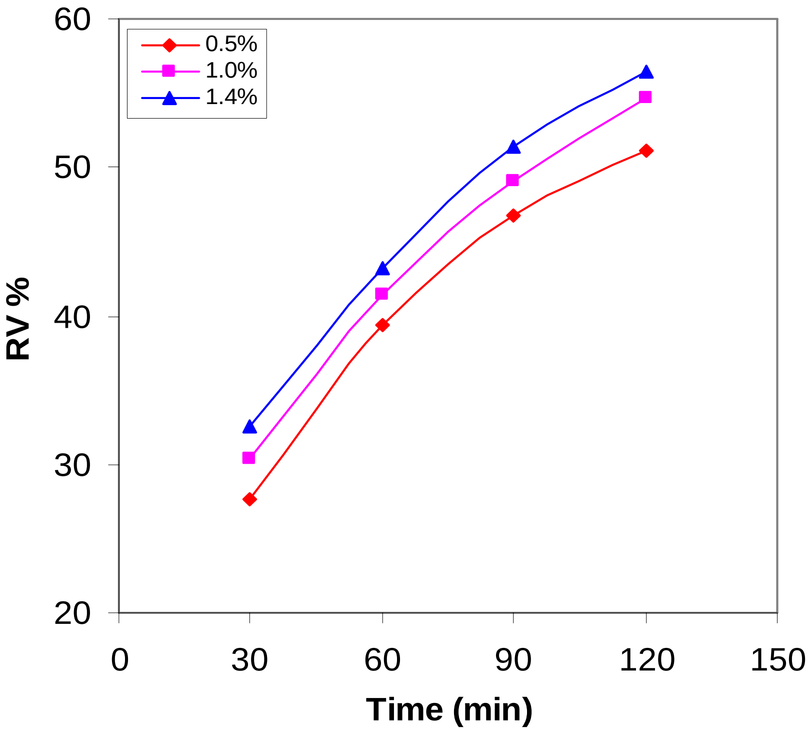


Figure (4.26) Percentage viscosity reduction vs. time for Oppanol B-200 solution at 1800 rpm

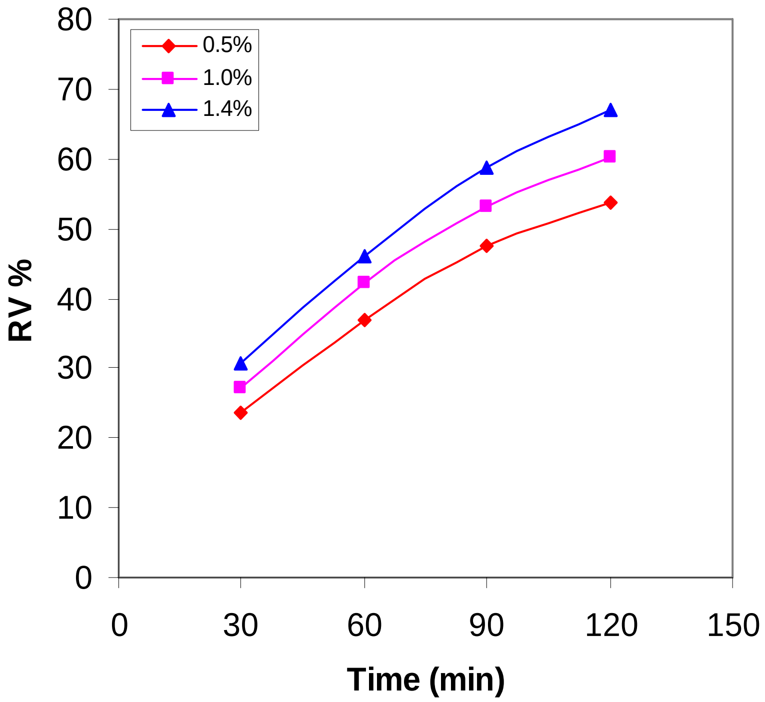


Figure (4.27) Percentage viscosity reduction vs. time for Oppanol B-250 solution at 1800 rpm

4.2.1.3 Molecular weight effect

It is well expected that the viscosity of Oppanol B solutions increase as molecular weight of polymer increases, as shown in figure (4.28). The viscosity of 1.0w/v% solutions as an example of Oppanol B 150 (Mw = $2.5*10^6$ g/mole), B 200 (Mw = $4.1*10^6$ g/mole) and B 250 (Mw = $5.9*10^6$ g/mole) are 44.8cp, 83.1cp and 293cp respectively. Moreover the viscosity of polymeric solution is usually a function of concentration as shown in figure (4.28). As in case of Oppanol 250, the viscosity of 0.5, 1.0 and 1.4w/v% solutions are 63.2cp, 293cp and 623cp respectively.

Solutions of three different molecular weights Polyisobutylene were exposed to mechanical degradation by high speed stirrer in order to investigate the effect of polymer molecular weight on viscosity changes by mechanical shearing. Figure (4.29) shows the effect of stirring speed on the variation of the viscosity for 1.4 % solutions of Oppanol B, 150, 200 and 250 having molecular weights 2.5, 4.1 and 5.9millions g/mole respectively. The results indicate that the viscosity of highest molecular weight Oppanol 250 was more sensitive to stirring speed, than Oppanol 150 and 200. The viscosity of 1.4w/v% solution decreases gradually as stirring speed increases. The viscosity of these solutions were 120cp, 231.9cp and 623cp for Oppanol B 150, 200 and 250 polymers respectively before stirring exposure. While after 2hr stirring at 1800rpm, there viscosity was changed to 81.7, 100.8 and 205.3cp respectively. These results indicate that 31.9%, 56.5% and 67.1% percent decrease of the viscosity for the three Oppanol polymers respectively. This observation indicates clearly that the largest changes in the viscosity due to mechanical degradation occur with the polymer of highest molecular weight. The polymer chains having different molecular weight will show different time dependent resistance. In other words longer molecules are more susceptible to mechanical degradation accompanying more rapid degradation.

Figure (4.30) show the effect of degradation by mechanical stirring on the viscosity of the three Oppanol polymers. The experiments were carried out on 1.4 w/v% polymeric concentration, 1800rpm stirring for 2hours. It can be concluded from this figure that a gradual lowering of viscosity is observed with increasing the exposure time due to mechanical degradation. At 60min stirring, the viscosity changed dramatically from 120, 231.9, 623cp to around 96.6, 132.3 and 339.1cp for Oppanol B 150, 200 and 250 respectively. Therefore, the highest molecular weight polymer undergoes faster degradation leading to higher lowering in viscosity than the lower molecular weight polymers such as B 150.

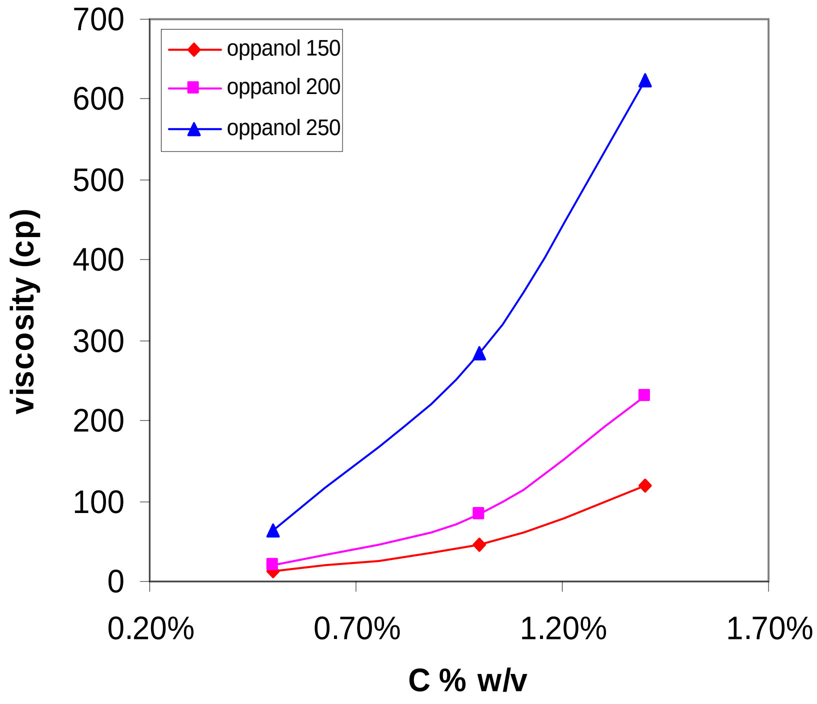


Figure (4.28) Combined effect of concentrations and molecular weight on the viscosity of Oppanol B solutions

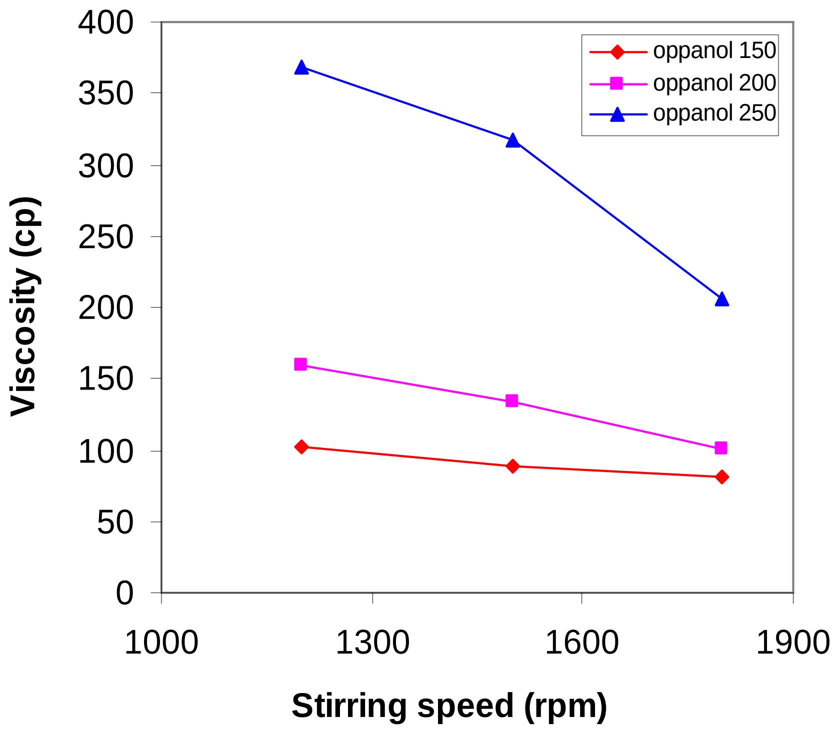


Figure (4.29) Viscosity changes as function of mechanical stirring speed and polymeric molecular at 1.4 w/v % solutions, 2hr exposure time

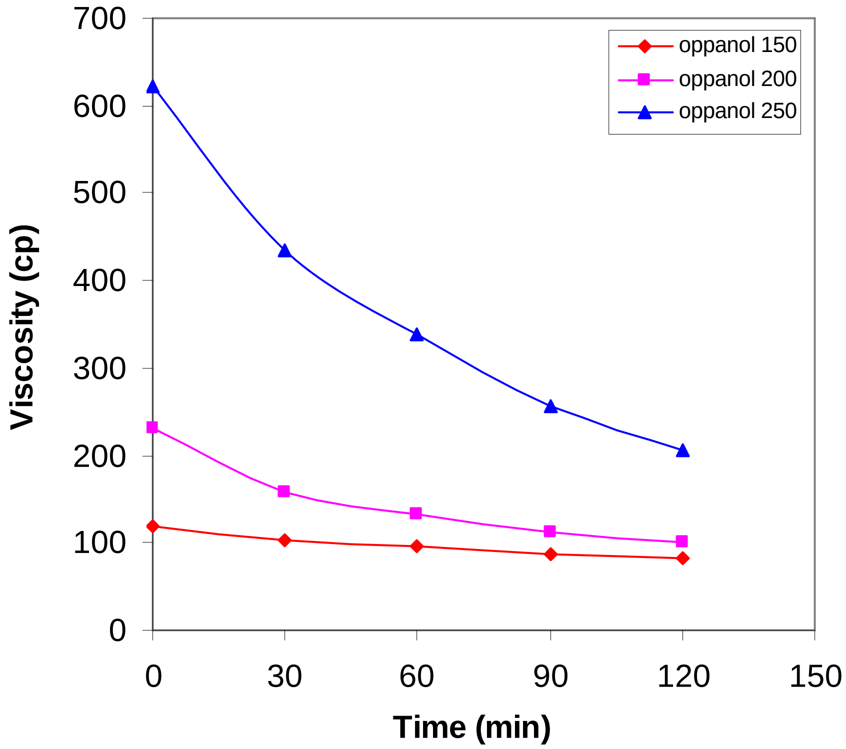


Figure (4.30) Viscosity variation of Oppanol B polymers by exposing 1.4 w/v % solutions to mechanical stirring at 1800rpm

4.2.2 Density changes

Figure (4.31) shows the densities of solutions at different concentrations for the three considered polymers. As it is expected, the density of polymeric solutions increases as the molecular weight of polymers increases as well as the concentration increases, as shown in figure (4.31). Thus, at 1.0w/v% concentration the density values are 0.794, 0.796 and 0.804g/cm^3 for Oppanol B polymers, 150, 200 and 250 respectively. Furthermore, the effect of concentration is shown in case of Oppanol B 250 as an example, resulted in 0.798, 0.804 and 0.808 g/cm^3 for concentrations 0.5, 1.0 and 1.4w/v% respectively.

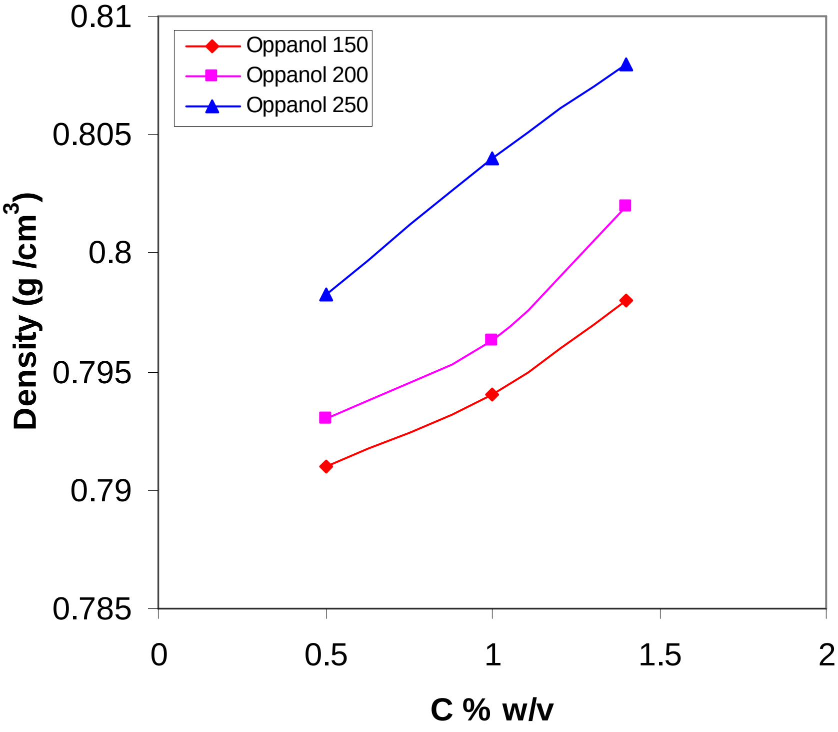


Figure (4.31) Density vs. concentration of Oppanol B polymers solutions in kerosene

Figures (4.32), (4.33) and (4.34) summarized the effect of shearing by 1800rpm stirring on density variation for Oppanol B 150, 200 and 250 at selected 1.4w/v% concentration. The density of the polymeric solutions decreases gradually with exposure time. The effect of stirring speed on lowering of the density is noticeable shown in these figures. The density behavior of 1.4w/v% Oppanol B 250 solution is taken as an example to explain the stirring effect. Thus, the density of original solutions is 0.808 g/cm^3 decreases to 0.799, 0.797 and 0.793g/cm^3 by shearing with 1200, 1500 and 1800rpm stirring for 2hr respectively as shown in figure (4.34).

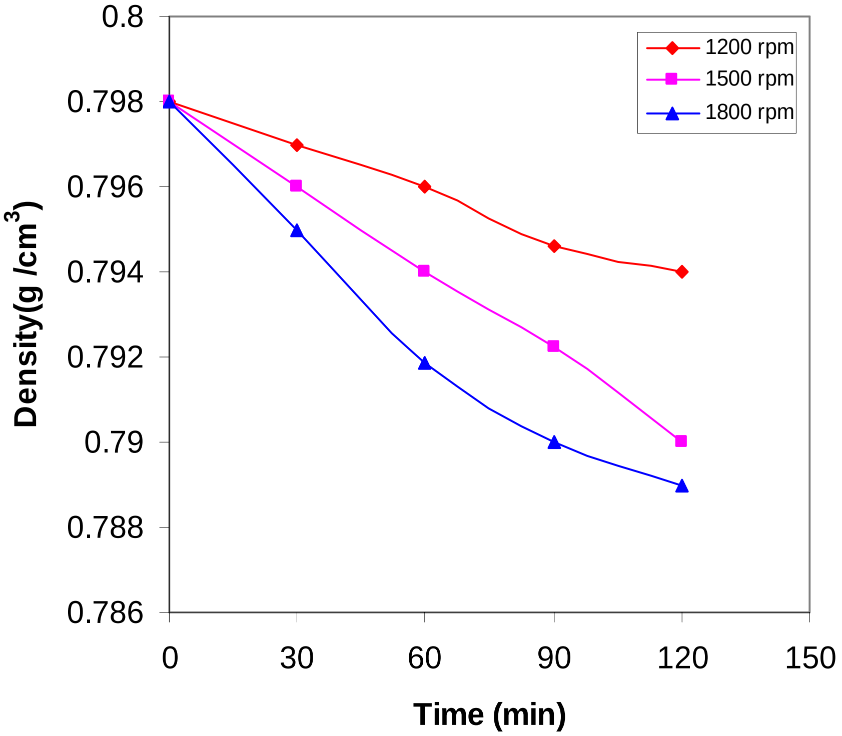


Figure (4.32) Effect of exposure time on the density of 1.4% Oppanol B-150 solution

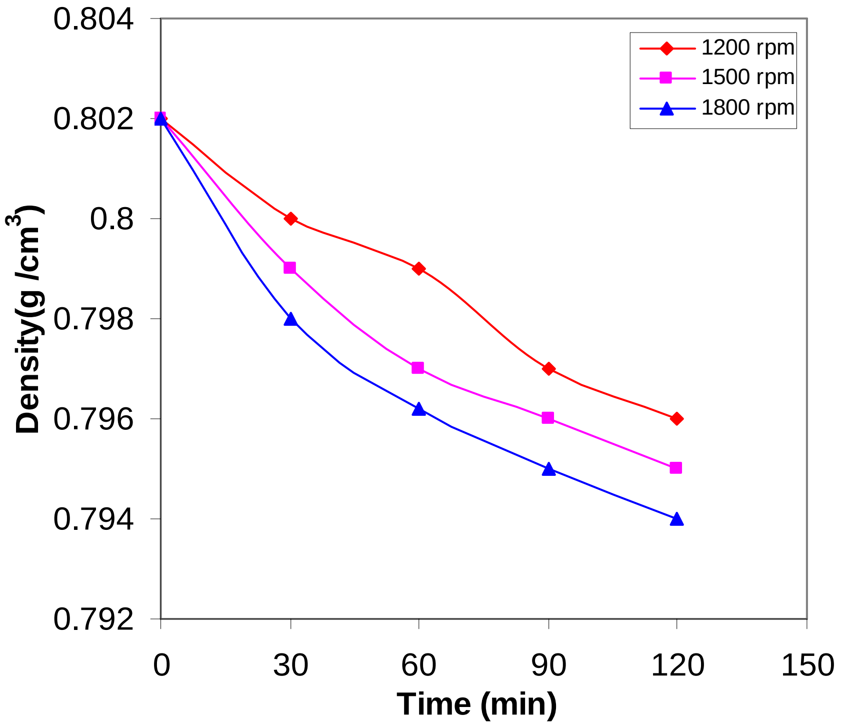


Figure (4.33) Effect of exposure time on the density of 1.4 % Oppanol B-200 solution

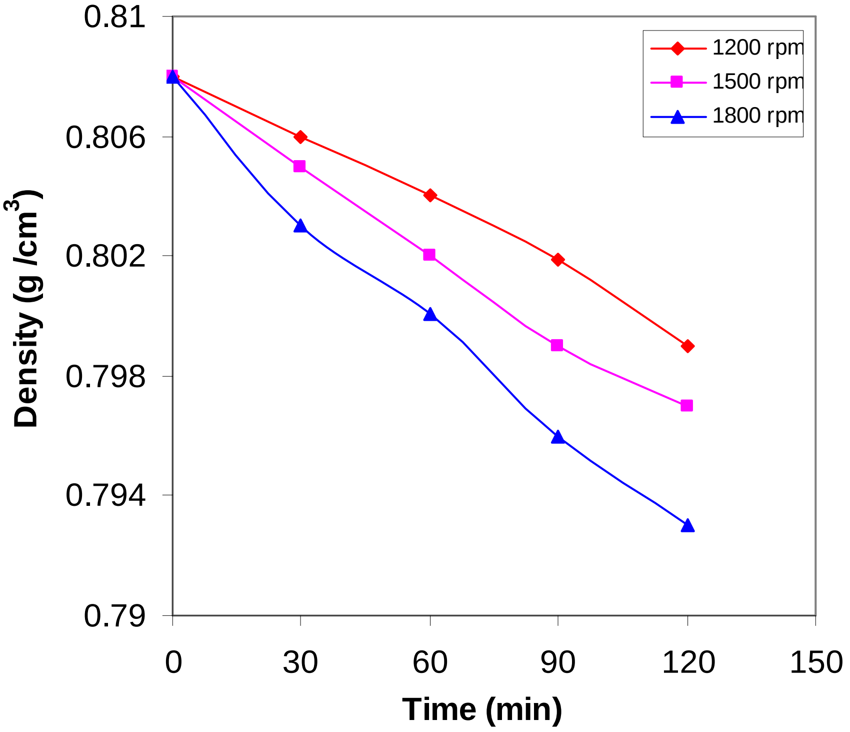


Figure (4.34) Effect of exposure time on the density of 1.4 % oppanol B-250 solution

The combined effect of concentration and shearing time on the density changes of polymer solutions are illustrated in figures (4.35), (4.36) and (4.37) for Oppanol B 150, 200 and 250 respectively. The results indicate that a similar behavior of density lowering was observed for the three polymers. This is in a good agreement with the observation of the viscosity changes due to mechanical degradation, as reported in figures (4.22), (4.23) and (4.24) previously.

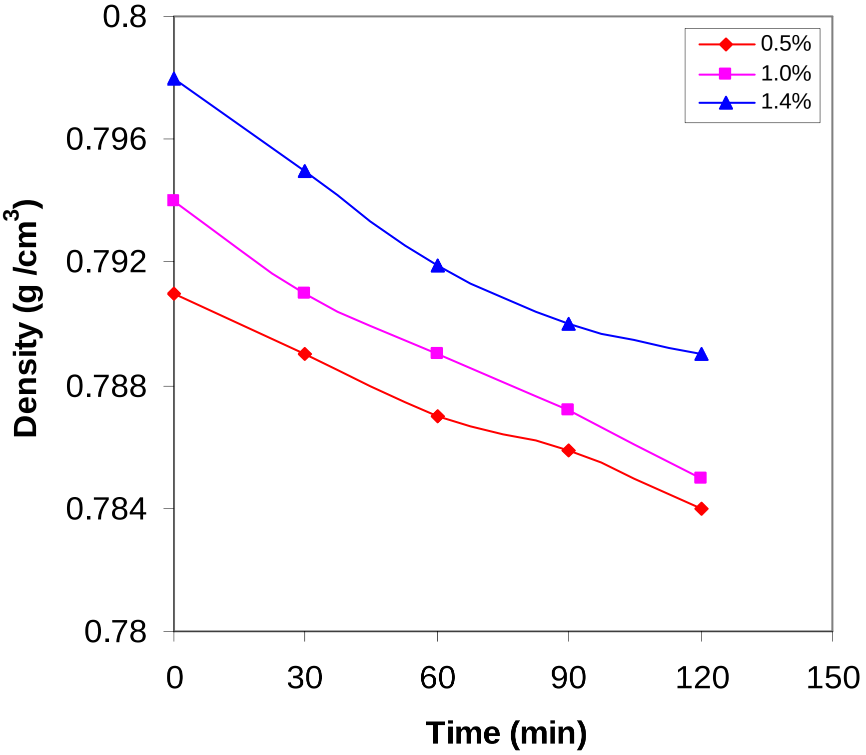
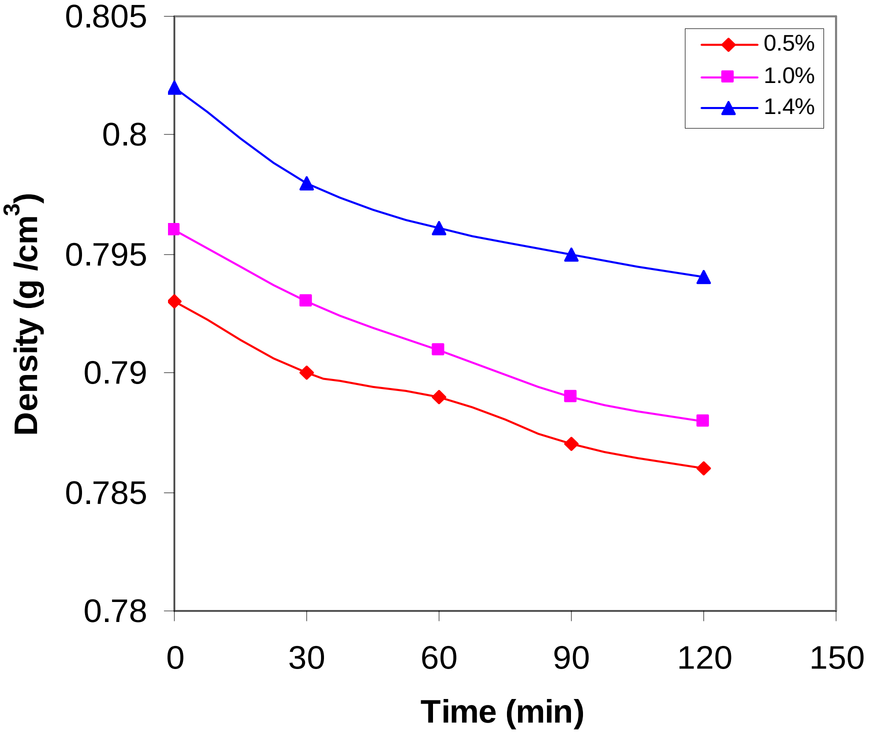


Figure (4.35) Concentration effect on density for Oppanol B-150 solution at 1800 rpm



Figure(4.36) Concentration effect on density for Oppanol B-200 solution at 1800 rpm

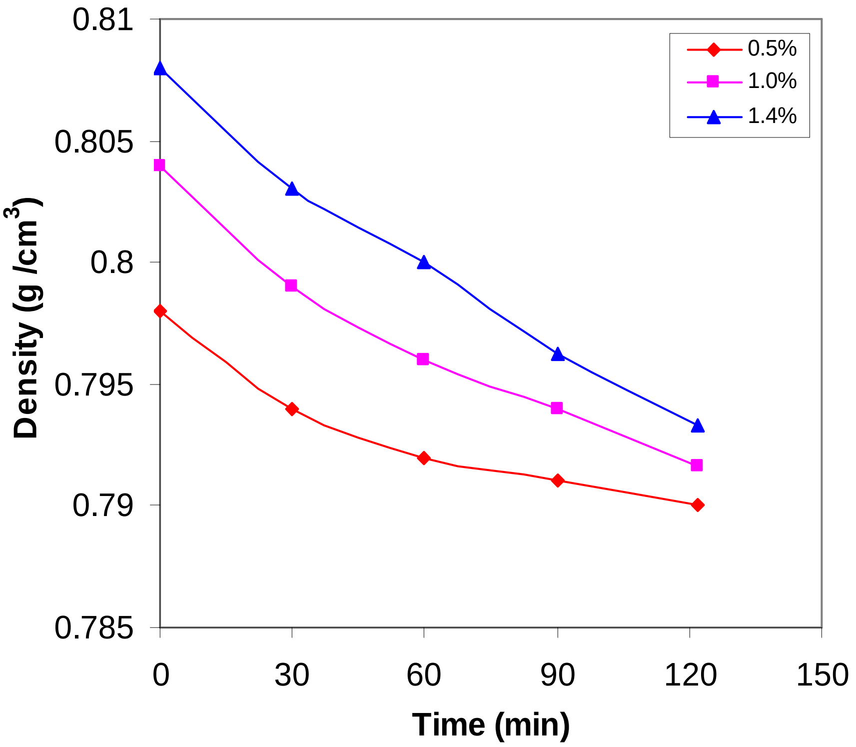


Figure (4.37) Concentration effect on density for Oppanol B-250 solution at 1800 rpm

4.3 Effect of degradation on drag reduction effectiveness of Oppanol additives

Effective polymeric drag–reduction additives are considered to be flexible, linear with high molecular weight(4). However the usage of these polymers is limited to their susceptibility to flow induced by shear degradation(5). Therefore , molecular degradation is one of the major defects in drag–reduction applications, since the polymeric additives are exposed to strong turbulent elongation strain and shear stress(7).

As illustrated adequately in the previous section (4.2), the viscosity of Oppanol B polymers undergo remarkable reduction by exposure there solutions to high speed mechanical stirring. Therefore it was worthy to compare the results of shear degradation by stirring of the three Oppanol polymers solution with the values of time dependence drag–reduction efficiency. Since the long chain polymers experience mid–point degradation, leading to the fact that the molecular chains having different molecular weights will show different time dependent resistance. Therefore, the study included, Oppanol B 150, B 200 and B 250 with average molecular weight of 2.5, 4.1 and 5.9 millions g/mole respectively.

The drag–reduction results were taken from previous published work of experimental data in gas oil circulation piping loop using the above Oppanol B types(24). The time dependence drag–reduction results for these polymers are shown in figure (4.38) which were carried out at 6.0m^3/hr flow rate in 31.75mm I.D pipe(24).

As shown in figure (4.38) the low molecular weight polymers are sharply degraded within the first hour resulting in fast decrease of percentage drag–reduction. While the higher molecular weight polymer has higher resistance towards the degradation. Therefore in case of Oppanol B 250 additive, still about 9% drag reduction was achieved after 210min operation due to presence of undegradable molecules, which act as drag reducer agents. The low molecular weight polymer B 150 was completely vanished after about one hour circulation leading to minor DR, while B 250 shows little drag–reduction effectiveness after 210min circulation. It was observed previously in section 4.2.2.1 that exposure of Oppanol B, 150, 200 and 250 polymeric solutions to high speed stirring, (1800rpm) leading to noticeable decrease in viscosity due to mechanical degradation.

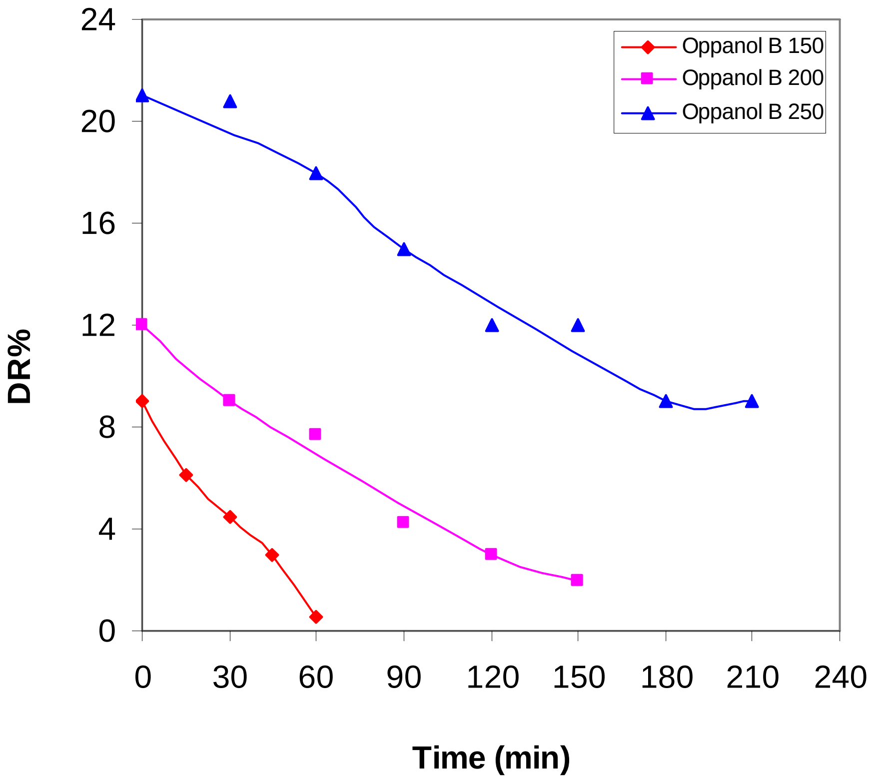


Figure (4.38) Effect of molecular weight on degradation of Oppanol B additives, at Q= 6 m^3/hr, 50 ppm concentration and 31.75 mm I.D

The results of Oppanol B 250 at different concentrations are plotted in figure (4.39) for 31.75mm I.D pipe at flow rate 6m^3/hr taking the time zero for maximum drag reduction(24). This figure indicates clearly that low concentrations will be degraded quickly compared with high concentration i.e 50ppm therefore the percentage DR decrease rapidly reaching to zero value after 60min and 120min running for 10ppm and 30ppm concentration respectively as shown in this figure. While at 50ppm concentration there is still undegraded polymer until 220 min experimental time elapsed. Since degradation is generally attributed to mechanical breaking of the polymer chains and when a low concentration exists in the pipe a larger performance of chains are destroyed and consequently a rapid decrease in the effective drag reduction is noticed. While, for high concentrations i.e 50ppm there is still sufficient effective polymer left to cause drag reduction at the considered experimental time.

As already reported previously in section 4.2 the largest lowering in the solution viscosity of Oppanol polymers due to mechanical degradation occur with polymeric solution of highest concentration, as shown in figure (4.24) for type B 250 polymer. Thus, the viscosity of Oppanol B 250, decreases from 63.2cp before mechanical stirring to about 29.3cp, 293cp to 116.3cp and 623cp to 205.3cp after exposure time of 2hr for solutions of 0.5, 1.0 and 1.4 w/v % concentrations respectively. Therefore the results in figure (4.39) is in agreement with those shown in figure (4.24) for the dependence of drag reduction effectiveness on the molecular polymer degradation.

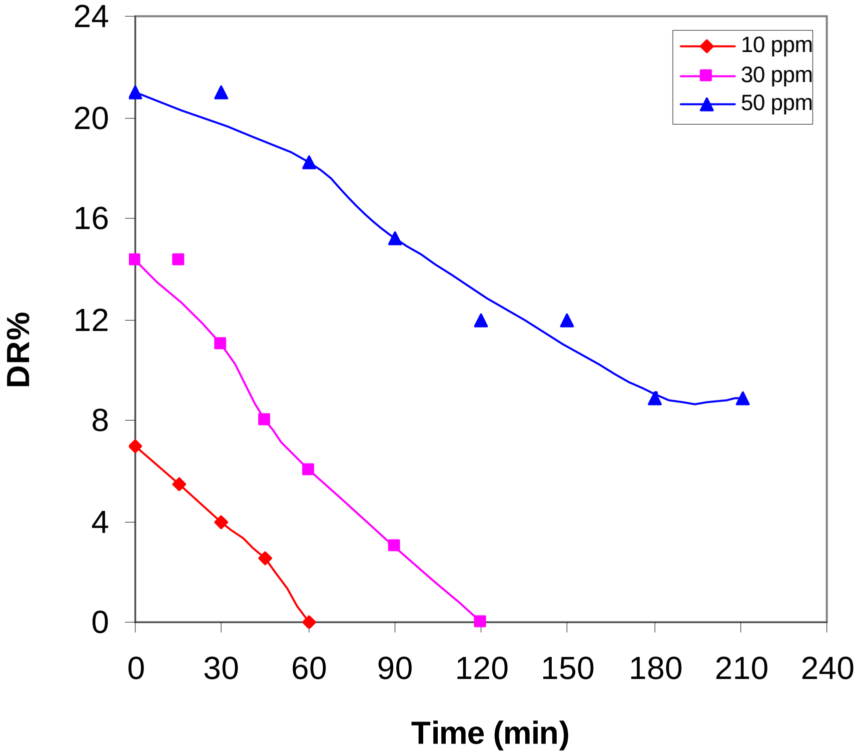


Figure (4.39) Time dependence of percentage drag-reduction for Oppanol B 250 at different concentration, 6 m^3/hr flow rate and 31.75 mm I.D

4.4 Mechanical degradation of Xanthan Gum

Xanthan Gum (XG) as a water soluble polysaccharide polymer is considered to be an effective drag–reducer agent in turbulence flow of hydrocarbons and water solvents(42). Hence, it was worthy to investigate the shear stability of XG toward mechanical forces and its effect on drag reduction performance. Therefore, XG water solutions of 0.5 and 1.0w/v % concentrations were exposed to shear degradation by mechanical stirring at 1200, 1500 and 1800rpm. The results of time dependence of viscosity changes at different conditions are illustrated in figure (4.40) through (4.43).

Figures (4.40) and (4.41) show a gradual decrease of the viscosity with exposure time and stirring speed for both solution concentrations due to degradation of XG polymers. While, figures (4.42) and (4.43) indicate the combined effect of exposure time and stirring rate on percentage lowering of the viscosity. The original viscosity of 0.5w/v% solution was 54.9cp decrease to 48.3, 46.2 and 44.3cp at shearing with 1200, 1500 and 1800rpm stirring rate respectively at 4hr exposure time. These are equal around 12.02, 15.85 and 19.31% decrease respectively. The corresponding values for 1.0% concentration of 276.2 cp (original) are 239.8cp (13.18%), 219.6cp (20.49%) and 200.8cp (27.29%) respectively as given in table (4.3). These indicate that the degradation increases as XG concentration increases.

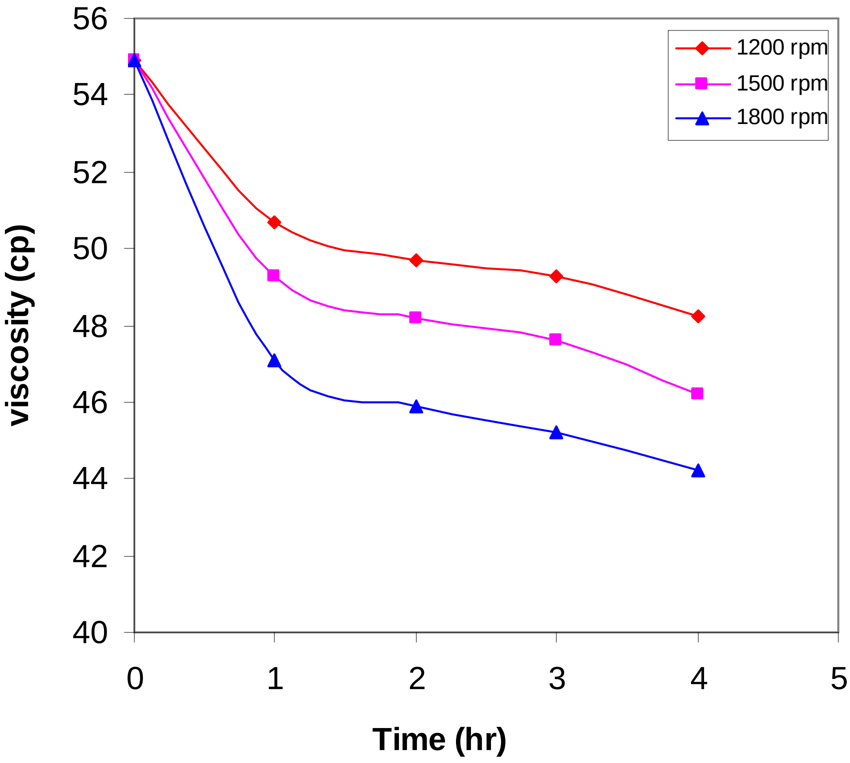


Figure (4.40) Effect of stirring rate on viscosity change of 0.5% XG solution at different time

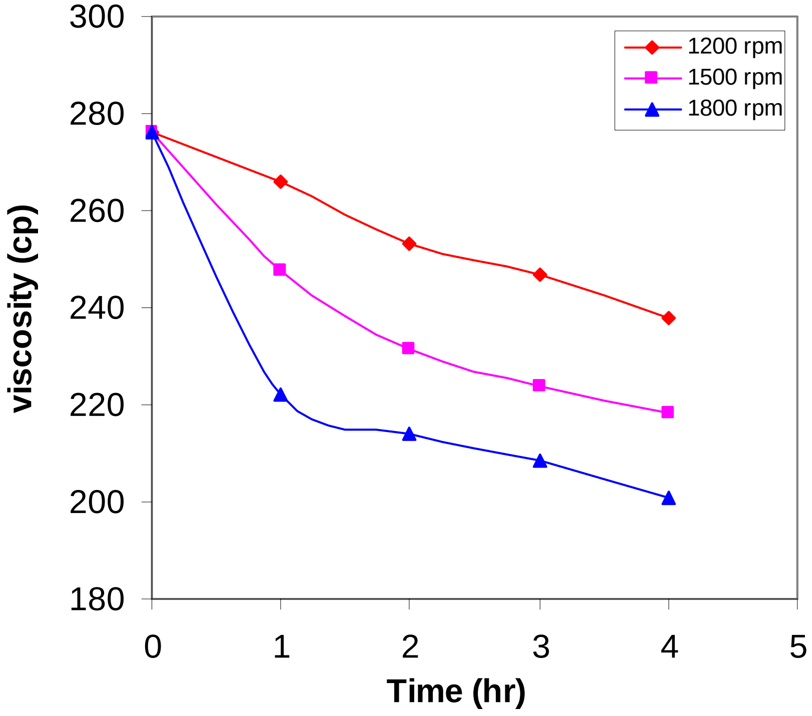


Figure (4.41) Effect of stirring rate on viscosity change of 1.0 % XG solution at different time

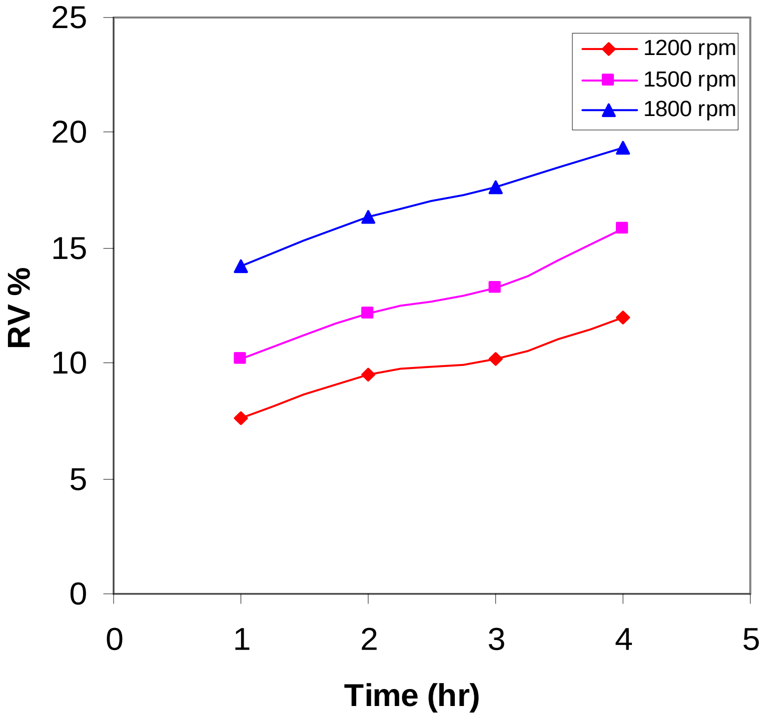


Figure (4.42) Effect of stirring rate on percent viscosity lowering of 0.5 % XG solution at 1800 rpm

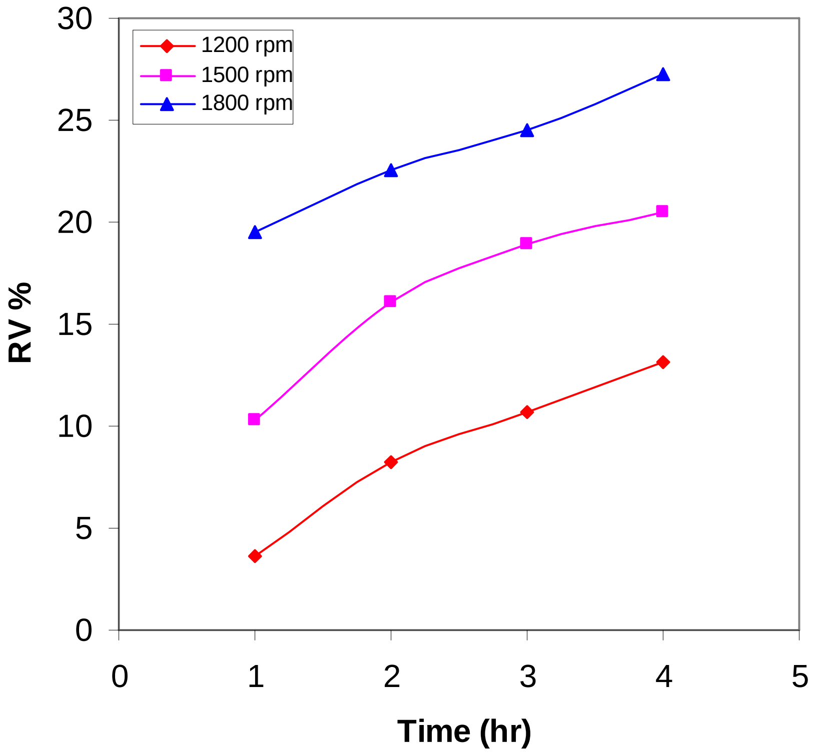


Figure (4.43) Effect of stirring rate on percent viscosity lowering of 1.0 % XG solution at 1800 rpm

Table (4.3) Viscosity and density variation of 0.5% and 1.0% XG solutions by exposure to shearing at different stirring rate and 4 hr time

Concentration w/v %		rpm			
		–	1200	1500	1800
0.5	μ (cp)	54.9	48.3	46.2	44.3
	% RV	–	12.02	15.85	19.31
	ρ (g/cm^3)	1.0102	1.0096	1.0094	1.0092
1.0	μ (cp)	276.2	239.8	219.6	200.8
	% RV	–	13.18	20.49	27.29
	ρ (g/cm^3)	1.0117	1.0113	1.01105	1.0108

As already observed previously in section 4.2, the high molecular weight Oppanol B polymers are less stable against mechanical shearing. High reduction in the viscosity of there solutions were noticed by high speed stirring, as shown in table (4.4) for 2hr exposure time at 1800rpm. The viscosity lowering of 0.5 and 1.0w/v% solutions of the highest molecular weight B 250 ($5.9*10^6$ g/mole) were 53.6% and 60.3% respectively. While the corresponding data for the lowest molecular weight type B 150 ($2.5*10^6$ g/mole) were 18.8% and 28.7% respectively and for XG solutions ($5.0*10^6$ g/mole) were 16.39% and 22.55% respectively. These results support the fact that the XG polymer is less sensitive to degradation by mechanical stirring than Oppanol B polymers. Kenis(47) reported a greater shear stability for XG than for a number of drag-reducing polymers. The stability to shear degradation decreased in the order, PAM > XG > PEO > GG > PIB.

Table (4.4) Percent viscosity changes of Oppanol B and XG polymers solutions by exposure to mechanical stirring, at 1800rpm and 2hr

Polymers	B 150	B 200	B 250	XG
Mw , million g/mole	2.5	4.1	5.9	5.0
%RV , 0.5 w/v% solution	18.8	51.1	53.6	16.39
%RV , 1.0 w/v% solution	28.7	54.7	60.3	22.55

A gradual decrease in the density of XG solutions was noticed during the shearing to high speed stirring as shown in figures (4.44) and (4.45). The density of 0.5 and 1.0 w/v% XG solutions are about 1.0102 and 1.0117 g/cm^3 respectively, which are greater than for Oppanol B polymers, due to the polarity of XG polymer and water is more dense than kerosene solvent.

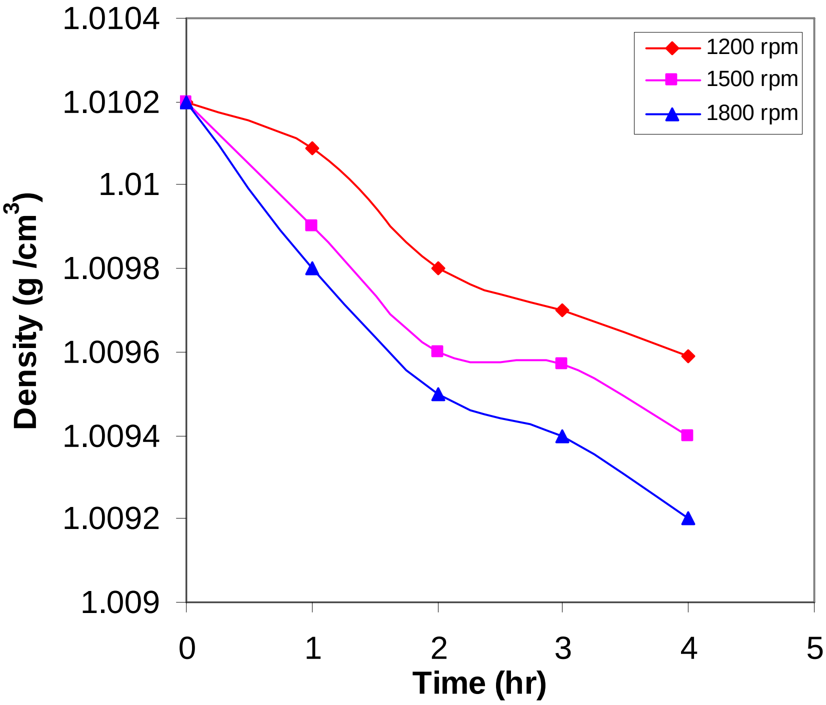


Figure (4.44) Effect of stirring rate on density change of 0.5% XG solution

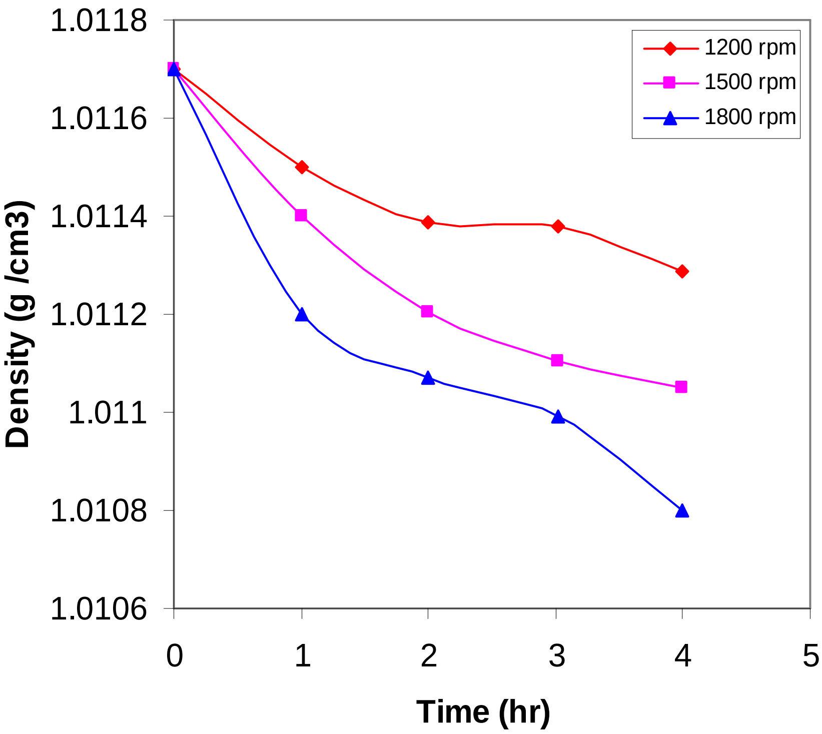


Figure (4.45) Effect of stirring rate on density change of 1.0 % XG solution

4.5 Drag reduction by XG additive

4.5.1 Effect of concentration and flow rate

A set of experiments were conducted on turbulent circulation of water to investigate the effectiveness of Xanthan gum as drag–reducer agents. The study was carried out at different XG concentrations, ranging 50–200 ppm and flow rates, 2.8, 4.4 and 6 m^3/hr, as illustrated in figure (4.46). This figure show that DR increases as polymer concentration increases. This phenomenon can be explained by the elastic sublayer model theory of Virk$^{(87)}$. This sublayer starts to grow with increasing additive concentration.

The results show, that within the range of additive concentrations, a gradual increase of percentage drag–reduction was observed by increasing the concentration within a certain flow rate and that means increasing the turbulence spectrum that is under the drag reducer effect. Thus, at 6m^3/hr flow rate, a 8.6 % drag–reduction was achieved by addition of 50ppm XG, increased to about 19.35 % for 200ppm, as an example.

One of the interesting factors in the study of drag reduction phenomena is the effect of flow rate on percentage drag reduction and its relation to turbulency and the effectiveness of XG as drag reducer. The flow rate effect was investigated at 2.8, 4.4 and 6m^3/hr as shown in figure (4.46). It is noticed that %DR is increased as flow rate increases. Increasing the flow rate means increasing the velocity which was represented by the dimensionless form of Reynolds number (Re) as shown in figure (4.47). That means increase the degree of turbulence inside the pipe, which will provide a better media to the drag reducer to be more effective. However, it is well known that the

To show the effect of turbulence on percentage drag reduction, 200ppm concentration is taken as an example. Thus, 12.03%, 15.88% and 19.35% drag reduction were observed by increasing Reynolds number in the order 22225, 40005 and 66675 respectively as shown in figure (4.47) .

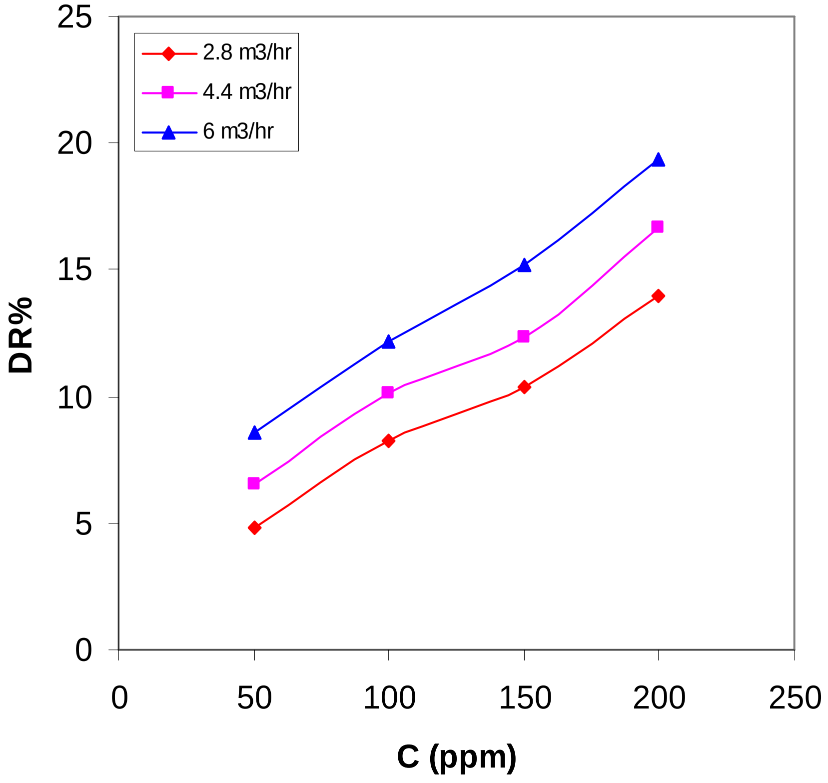


Figure (4.46) Effect of concentration and flow rate on percent drag reduction for XG additive

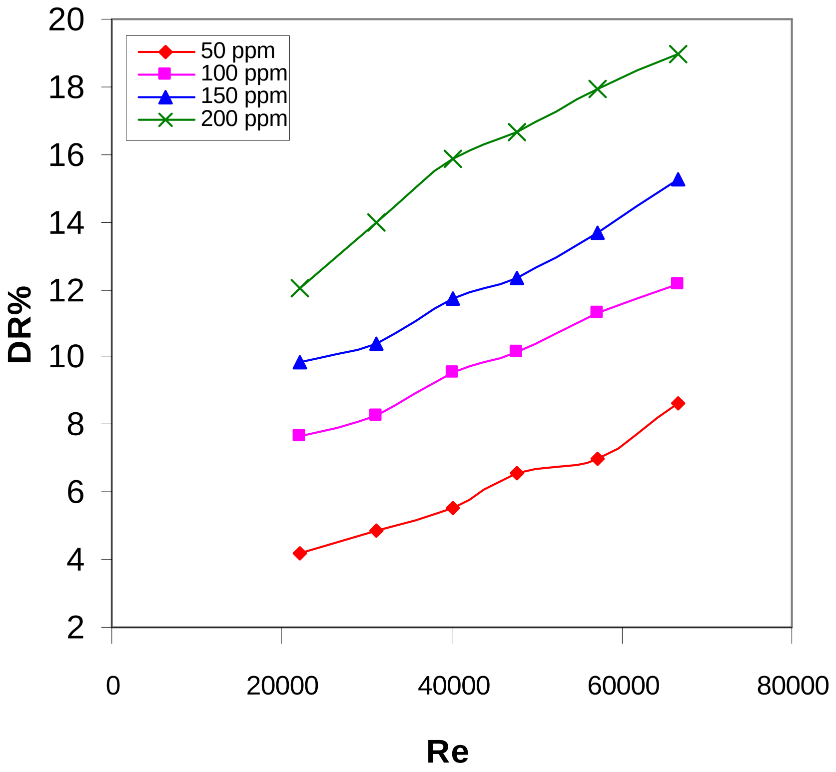


Figure (4.47) Reynolds number dependence of drag reduction for XG additive

4.5.2 Time dependence

The drag–reduction effectiveness of Xanthan gum additive during water turbulent circulation in piping system was studied in order to investigate its resistance to shear degradation. The results of the percentage drag reduction as a function of the circulation time recorded up to 7hr at flow rate 6m^3/hr are shown in figure (4.48) for different concentrations. A gradual decrease of percent drag–reduction was observed at time progress due to the degradation of polymer molecules under turbulent flow. The DR behaviour in turbulent flow is appeared to be related to shearing force in which these cause the breakage of main chain of the polymer by the mechanical energy. Therefore DR decrease with time as a consequence of scission of polymeric chain caused by turbulence flow.

Furthermore the time dependence drag–reduction results show that XG additive has noticeable lower tendency to degradation in turbulence flow than Oppanol B additives. The maximum percentage decrease in values of %DR was about 57.06% for XG additive at 100ppm concentration and 6 m^3/hr flow rate after 7hr circulation. While the DRE of Oppanol B 150 was complete degrade at about one hour flowing and Oppanol B 200 was sharply degraded after about two hours. The high molecular weight B 250 was lost about 57.14% of its efficiency at 3.5hr processing as shown in figure (4.38). This observation is in agreement with the results of exposing of XG solution to mechanical stirring and support the fact that XG solutions are more stable against mechanical shearing than the high molecular weight Oppanol polymers.

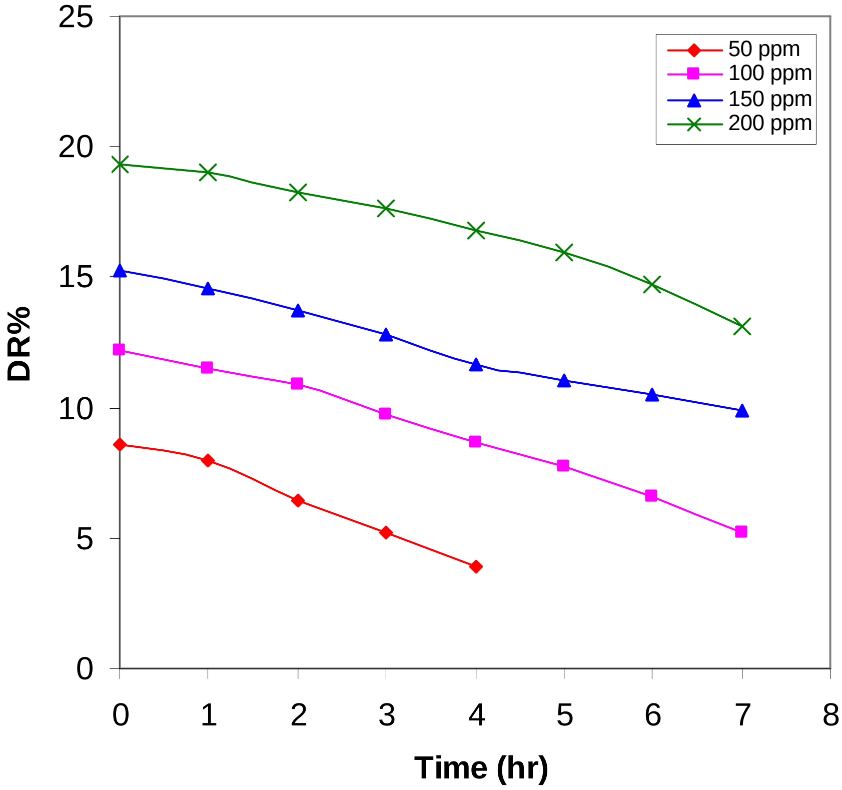


Figure (4.48) Effect of concentration on degradation for XG at 6 m^3/hr and 31.75 mm I.D

Figure (4.49) shows the shear stability of XG in terms of the relative drag reduction, DR/DR_0 ratio as a function of time for solutions of XG of concentrations 50, 100, 150 and 200ppm. DR/DR_0 represents the ratio of percent drag reduction efficiency at time (t) to drag reduction at t=0. DR/DR_0 examined with $6m^3/hr$ at four concentrations, the relative drag reduction dropped from 1 before degradation to about 0.43 after 7hr circulation time for concentration 100ppm. The corresponding values for concentrations 150 and 200ppm were 0.65 and 0.68 respectively. These supported the fact that as the concentration increases the degradation ability decreases as shown in figure (4.49).

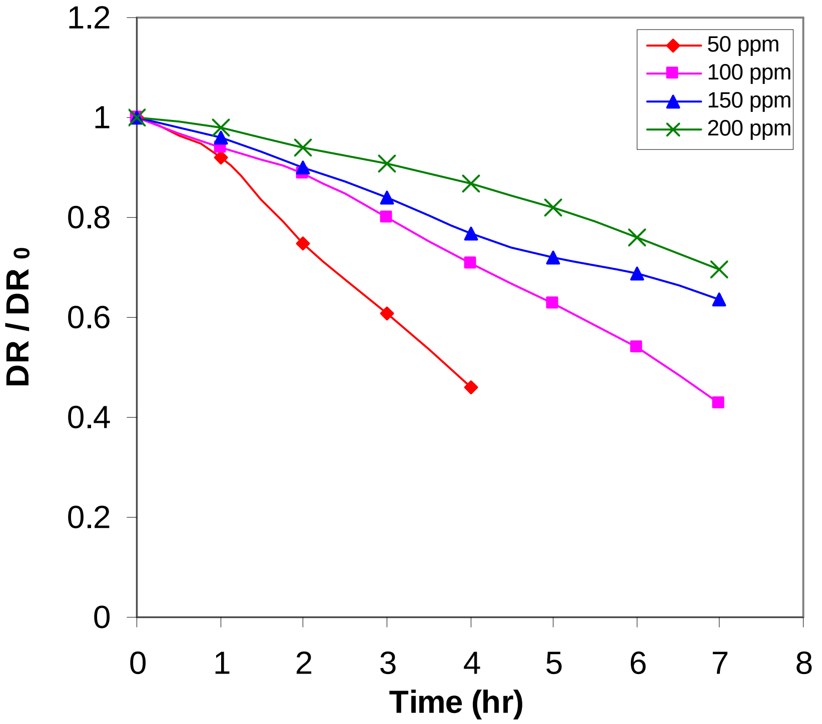


Figure (4.49) DR/DR_0 as a function of time for XG solution

Chapter Five

Conclusions and Recommendations for further work

5.1 Conclusions

1. The shear degradation behaviour of Polyisobutylene drag–reducer agents with three different molecular weights (2.5, 4.1 and 5.9 million g/mole) was studied by exposing their solutions to high speed mechanical stirring.

2. It was observed that susceptibility of PIB to degradation increases with increasing the stirring speed, polymer molecular weight and increasing of concentrations. Moreover the polymer degraded rapidly during the early stages of stirring and then degradation occurs gradually. Also Viscosity lowering was observed by expose of XG solutions to high speed stirring due to molecular shear degradation. The degradation increases also with increasing the stirring speed, exposure time and increasing of concentrations.

3. The drag – reduction efficiency of Polyisobutylenes of three different molecular weights decreases dramatically with time due to shear degradation of polymer molecules under the exposed turbulent recirculation flow. The behaviour of molecular degradation during the drag–reduction experiments are in agreement with the observation for shear degradation by stirring.

4. The high molecular weight PIB polymers show a good drag–reduction effectiveness at concentrations below 50ppm in turbulent pipe flow.

While, Xanthan gum is relatively poor drag–reducing agent. It requires much higher concentrations (200ppm) to cause an efficient drag reduction.

6. Xanthan gum additive as a rigid polysaccharide shows more shear stability than the flexible PIB polymers by turbulent drag–reduction investigations.

5.2 Recommendations for further work

1. Further work can be carried out to prepare solutions of other types of drag reducers such as Polyethylene oxide and Polyacrylamide as water soluble polymers in addition to studying their rheological properties and drag reduction effectiveness.

2. Studying the effect of solvent type on both shear degradation and turbulent drag–reduction effectiveness of high molecular weight polymer additives.

3. Investigating the effect of temperature and radiation energy on chemical degradation of high molecular weight drag–reducer agents.

4. An obvious area for future work is to study the effect of mechanical configuration of piping flow loop, such as elbows, inclined pipes and type of circulation pump on effectiveness of polymeric drag–reducer agent and their molecular degradation.

5. Develop a correlation between drag–reduction efficiency and shear degradation of polymer additives at various flowing conditions.

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Appendix

Appendix A

Shear degradation of dissolved Oppanol−B polymers

Table (A-1) Effect of stirring speed on the some properties of Oppanol–B 150 dissolved in kerosene, 0.5 w/v %

Stirring speed (rpm)	t (min)	μ (cp)	%RV	ρ (g/cm^3)
1200	0	11.82		0.791
	30	11.53	2.5	0.790
	60	11.21	5.1	0.789
	90	10.98	7.1	0.788
	120	10.8	8.6	0.787
1500	0	11.82		0.791
	30	11.07	6.3	0.790
	60	10.72	9.3	0.788
	90	10.39	12.1	0.787
	120	10.03	15.1	0.786
1800	0	11.82		0.791
	30	10.82	8.5	0.789
	60	10.27	13.1	0.787
	90	10.01	15.3	0.786
	120	9.61	18.8	0.784

Table(A-2) Effect of stirring speed on the some properties of Oppanol−B 150 dissolved in kerosene, 1.0 w/v %

Stirring speed (rpm)	t (min)	μ (cp)	%RV	ρ (g/cm^3)
1200	0	44.8		0.794
	30	42.5	5.1	0.793
	60	39.2	12.5	0.791
	90	37.7	15.8	0.789
	120	34.3	23.4	0.788
1500	0	44.8		0.794
	30	41.2	8	0.792
	60	38.8	13.3	0.789
	90	36.2	19.2	0.788
	120	33.4	25.4	0.786
1800	0	44.8		0.794
	30	39.7	11.4	0.790
	60	37.2	16.9	0.789
	90	34.6	22.7	0.787
	120	31.9	28.7	0.785

Table(A-3) Effect of stirring speed on the some properties of Oppanol –B 150 dissolved in kerosene, 1.4 w/v %

Stirring speed (rpm)	t (min)	μ (cp)	%RV	ρ (g/cm^3)
1200	0	120		0.798
	30	116	3.33	0.797
	60	108.3	9.75	0.796
	90	105.9	11.75	0.7945
	120	102.6	14.5	0.794
1500	0	120		0.798
	30	112.8	6	0.796
	60	102.5	14.5	0.794
	90	97.2	19	0.792
	120	89.1	25.75	0.790
1800	0	120		0.798
	30	103.2	14	0.795
	60	96.6	19.5	0.792
	90	87.9	26.7	0.790
	120	81.7	31.9	0.789

Table (A-4) Effect of stirring speed on the some properties of Oppanol–B 200 dissolved in kerosene, 0.5 w/v %

Stirring speed (rpm)	t (min)	μ (cp)	%RV	ρ (g/cm^3)
1200	0	16.44		0.793
	30	14.64	10.95	0.792
	60	11.72	28.7	0.791
	90	10.93	33.5	0.7905
	120	10.26	37.6	0.790
1500	0	16.44		0.793
	30	12.87	21.7	0.791
	60	10.73	34.7	0.790
	90	9.47	42.4	0.789
	120	8.99	45.3	0.788
1800	0	16.44		0.793
	30	11.87	27.7	0.790
	60	9.96	39.4	0.789
	90	8.73	46.8	0.787
	120	8.04	51.1	0.786

Table(A-5) Effect of stirring speed on the some properties of Oppanol –B 200 dissolved in kerosene, 1.0 w/v %

Stirring speed (rpm)	t (min)	μ (cp)	%RV	ρ (g/cm^3)
1200	0	83.1		0.796
	30	76.4	8.1	0.796
	60	69.7	16.1	0.794
	90	61.2	26.4	0.793
	120	53.3	35.8	0.791
1500	0	83.1		0.796
	30	67.2	19.1	0.794
	60	58.5	29.6	0.792
	90	52.3	37.1	0.790
	120	45.7	45	0.790
1800	0	83.1		0.796
	30	57.8	30.4	0.793
	60	48.6	41.5	0.791
	90	42.3	49.1	0.789
	120	37.6	54.7	0.788

Table(A-6) Effect of stirring speed on the some properties of Oppanol –B 200 dissolved in kerosene, 1.4 w/v %

Stirring speed (rpm)	t (min)	μ (cp)	%RV	ρ (g/cm^3)
1200	0	231.9		0.802
	30	207.7	13	0.800
	60	181.5	21.7	0.799
	90	173.8	25.1	0.797
	120	159.9	31	0.796
1500	0	231.9		0.802
	30	182.3	21.3	0.799
	60	160.2	30.9	0.797
	90	148.2	36.1	0.796
	120	133.7	42.3	0.795
1800	0	231.9		0.802
	30	157.1	32.2	0.798
	60	132.3	42.9	0.796
	90	112.6	51.4	0.795
	120	100.8	56.5	0.794

Table(A-7) Effect of stirring speed on the some properties of Oppanol –B 250 dissolved in kerosene, 0.5 w/v %

Stirring speed (rpm)	t (min)	μ (cp)	%RV	ρ (g/cm^3)
1200	0	63.2		0.798
	30	57.7	8.7	0.797
	60	52.4	17.1	0.796
	90	47.8	24.4	0.794
	120	40.1	36.6	0.792
1500	0	63.2		0.798
	30	51.8	18	0.795
	60	44.2	30	0.794
	90	39.9	36.9	0.793
	120	34.8	44.9	0.791
1800	0	63.2		0.798
	30	47.2	24.8	0.794
	60	39.8	37	0.792
	90	33.1	47.6	0.791
	120	29.3	53.6	0.790

Table (A-8) Effect of stirring speed on the some properties of Oppanol–B 250 dissolved in kerosene, 1.0 w/v %

Stirring speed (rpm)	t (min)	μ (cp)	%RV	ρ (g/cm^3)
1200	0	293		0.804
	30	258.3	11.8	0.802
	60	230.8	21.2	0.801
	90	211.6	27.8	0.800
	120	194.2	33.7	0.797
1500	0	293		0.804
	30	236.5	19.3	0.801
	60	207	29.3	0.799
	90	186.1	36.5	0.798
	120	165.9	43.4	0.795
1800	0	293		0.804
	30	213.4	27.2	0.799
	60	169.6	42.1	0.796
	90	137.4	53.1	0.794
	120	116.3	60.3	0.792

Table (A-9) Effect of stirring speed on the some properties of Oppanol–B 250 dissolved in kerosene, 1.4 w/v %

Stirring speed (rpm)	t (min)	μ (cp)	%RV	ρ (g/cm^3)
1200	0	623		0.808
	30	552.7	11.3	0.806
	60	477.2	23.4	0.804
	90	409.2	34.3	0.802
	120	368.4	40.9	0.799
1500	0	623		0.808
	30	519.5	16.6	0.805
	60	423.3	32.1	0.802
	90	370.9	40.5	0.799
	120	317.1	49.1	0.797
1800	0	623		0.808
	30	434.9	30.7	0.803
	60	339.1	45.6	0.800
	90	256.5	58.8	0.796
	120	205.3	67.1	0.793

Appendix B
Shear degradation of dissolved Xanthan gum polymers

Table (B-1) Effect of stirring speed on the some properties of Xanthan gum dissolved in water, 0.5 w/v %

Stirring speed (rpm)	t (hr)	μ (cp)	%RV	ρ (g/cm^3)
1200	0	54.9		1.0102
	1	50.7	7.65	1.0101
	2	49.7	9.47	1.0098
	3	49.3	10.2	1.0097
	4	48.3	12.02	1.0096
1500	0	54.9		1.0102
	1	49.3	10.2	1.0099
	2	48.2	12.2	1.0096
	3	47.6	13.29	1.0096
	4	46.2	15.85	1.0094
1800	0	54.9		1.0102
	1	47.1	14.2	1.0098
	2	45.9	16.39	1.0095
	3	45.2	17.67	1.0094
	4	44.3	19.31	1.0092

Table (B-2) Effect of stirring speed on the some properties of Xanthan gum dissolved in water, 1.0 w/v %

Stirring speed (rpm)	t (hr)	μ (cp)	%RV	ρ (g/cm^3)
1200	0	276.2		1.0117
	1	266.1	3.66	1.0115
	2	253.3	8.25	1.0114
	3	246.8	10.64	1.0114
	4	239.8	13.18	1.0113
1500	0	276.2		1.0117
	1	247.8	10.28	1.0114
	2	231.7	16.11	1.0112
	3	224	18.89	1.0111
	4	219.6	20.49	1.01105
1800	0	276.2		1.0117
	1	222.3	19.51	1.0112
	2	213.9	22.55	1.0111
	3	208.6	24.48	1.0110
	4	200.8	27.29	1.0108

Appendix C

Time dependence of %DR effectiveness with PIB additive

Table (C-1) Effect of concentration on degradation of Oppanol–B 250 at 6 m^3/hr

t (min)	Concentration		
	10 ppm	30 ppm	50 ppm
0	7	14.3	21
15	5.5	14.3	—
30	4	11	21
45	2.5	8	—
60	0	6	18
90	—	3	15
120	—	0	12
150	—	—	12
180	—	—	9
210	—	—	9

Table (C-2) Effect of molecular weight on degradation of Oppanol–B at 50 ppm and 6 m^3/hr

t (min)	Oppanol −B 150	Oppanol −B 200	Oppanol −B 250
0	9	12	21
15	6	—	—
30	4.5	9	21
45	3	—	—
60	0.5	7.7	18
90	—	4.2	15
120	—	3	12
150	—	2.2	12
180	—	—	9
210	—	—	9

Appendix D
Time dependence of %DR effectiveness with XG additive

Table (D-1) Effect of mechanical degradation on percent drag reduction effectiveness of XG solution at 50 ppm

Q (m^3/hr)	DR (t=0)	DR(t =1hr)	DR(t =2hr)	DR(t =3hr)	DR(t =4hr)
6	8.6	7.95	6.45	5.23	3.94
5.2	6.99	6.42	5.75	4.69	3.21
4.4	6.57	6.35	5.22	4.49	3.09
3.6	5.51	5.29	4.98	3.82	2.94
2.8	4.85	5.16	4.65	3.23	2.02
6	4.20	4.93	3.91	2.89	1.45

Table (D-2) Effect of mechanical degradation on percent drag reduction effectiveness of XG solution at 100 ppm

Q (m^3/hr)	DR (t=0)	DR (t=1hr)	DR (t=2hr)	DR (t=3hr)	DR (t=4hr)	DR (t=5hr)	DR (t=6hr)	DR (t=7hr)
6	12.18	11.53	10.86	9.75	8.67	7.74	6.63	5.23
5.2	11.28	10.49	8.94	8.49	7.17	6.64	6.19	4.87
4.4	10.16	10.11	7.86	8.26	7.3	6.18	5.89	4.38
3.6	9.55	9.74	7.35	7.65	6.98	5.69	5.58	5.15
2.8	8.28	9.09	6.86	6.46	6.77	5.05	4.85	4.55
2	7.68	7.37	6.52	5.79	6.16	4.78	4.35	3.77

Table (D-3) Effect of mechanical degradation on percent drag reduction effectiveness of XG solution at 150 ppm

Q (m^3/hr)	DR (t=0)	DR (t=1hr)	DR (t=2hr)	DR (t=3hr)	DR (t=4hr)	DR (t=5hr)	DR (t=6hr)	DR (t=7hr)
6	15.23	14.55	13.76	12.83	11.68	11.02	10.50	9.86
5.2	13.65	12.30	11.06	11.37	10.18	9.73	9.16	8.14
4.4	12.36	11.24	10.67	9.89	9.27	8.99	8.03	7.3
3.6	11.76	9.93	10.44	9.26	8.09	8.31	7.79	6.84
2.8	10.40	9.29	8.78	7.98	7.37	7.68	6.97	5.96
2	9.85	8.69	8.11	7.25	6.96	6.52	6.09	5.36

Table (D-4) Effect of mechanical degradation on percent drag reduction effectiveness of XG solution at 200 ppm

Q (m^3/hr)	DR (t=0)	DR (t=1hr)	DR (t=2hr)	DR (t=3hr)	DR (t=4hr)	DR (t=5hr)	DR (t=6hr)	DR (t=7hr)
6	19.35	18.99	18.24	17.63	16.78	15.95	14.69	13.15
5.2	17.92	17.69	16.28	15.35	15.04	14.42	12.83	10.08
4.4	16.63	16.57	15.34	14.61	13.48	12.92	11.4	9.94
3.6	15.88	15.29	14.93	14.12	12.5	10.88	9.85	8.38
2.8	13.97	13.44	14.14	12.93	11.41	10.10	9.09	7.88
2	12.03	13.33	12.32	11.59	10.14	9.71	8.69	7.25

Table (D-5) Effect of mechanical degradation on the relative drag reduction of XG solution at different concentration and flow rate of 6m^3/hr

Time (hr)	50 ppm	100 ppm	150 ppm	200 ppm
0	1	1	1	1
1	0.92	0.94	0.96	0.98
2	0.75	0.89	0.9	0.94
3	0.61	0.8	0.84	0.91
4	0.46	0.71	0.77	0.87
5	—	0.63	0.72	0.82
6	—	0.54	0.69	0.76
7	—	0.43	0.65	0.68

الخلاصة

يحد الانحلال الميكانيكي للسلاسل البوليمرية من استخداماتها في تطبيقات تقليل الاعاقة في الجريان المضطرب. تم أختبار بوليمرات البولي أيزوبيوتلين عالية الوزن الجزيئي نوع (الاوبانول) بتعريض محاليلها الى خلاط ميكانيكي بسرع مختلفة لفترة زمنية تصل الى نحو ساعتين. شمل البحث ثلاثة انواع من الاوبانول نوع ١٥٠، ٢٠٠، ٢٥٠ ذات أوزان جزيئية مختلفة، ٢,٥، ٤,١، ٥,٩ مليون غم /مول على التوالي. تم قياس اللزوجة لمحاليل الاوبانول عند تراكيز٠,٥، ١,٠، ١,٤ % وزن/حجم أثناء الخلط ولفترات زمنية مختلفة.

بعد أجراء التجارب تم ملاحظة أن مدى التحلل يتأثر بالوزن الجزيئي وسرعة الخلاط والتركيز فالبوليمرات الطويلة السلسلة والخطية تكون أكثر تعرضاً للتحلل عند تعريض محاليلها للخلاط الميكانيكي. لذلك فأن أوبانول ٢٥٠ ذات الوزن الجزيئي العالي يكون أكثر حساسية للانحلال مقارنة بأوبانول ١٥٠ و ٢٠٠. كذلك عند زيادة السرع والتراكيز نلاحظ أن التحلل يزداد عند زيادة سرع الخلاط وزيادة تراكيز المحاليل.

عند تدوير محاليل البولي أيزوبيوتلين (نوع الاوبانول) ذات الاوزان الجزيئية المختلفة في منظومة تدوير الجريان المضطرب وحساب تقليل الاعاقة مع الزمن ومقارنة النتائج مع نتائج الانحلال بالخلاط الميكانيكي نلاحظ أن النقصان في تقليل الاعاقة مع الزمن ينطبق مع نتائج التحلل بتأثير الخلاط والذي يؤدي الى تقليل الوزن الجزيئي للمضافات البوليمرية المتمثل بنقصان اللزوجة عند تعريض المحاليل لسرع عالية ولفترات زمنية مختلفة.

تم أختبار نوع أخر من البوليمرات وهوXG بتعريض محلوله الى خلاط ميكانيكي أيضاً عند سرع مختلفة وعند تراكيز٠,٥، ١,٠%وزن/حجم ولفترة زمنية تصل الى ٤ ساعات . تم قياس اللزوجة أثناء الخلط لفترات زمنية مختلفة وتم ملاحظة أن محاليل XG تظهرأكثر ثبوتية من بوليمرات الاوبانول. وعند تدوير XG في منظومة التدوير عند تراكيز تصل الى ٢٠٠جزء/مليون وسرع جريان مضطربة مختلفة نلاحظ أن XG يعد عامل ضعيف لتقليل الاعاقة مقارنة بتركيز ٥٠جزء/مليون لمضاف الاوبانول ٢٥٠ عند نفس ظروف الجريان.

شكر وتقدير

وأنا أضع قلمي بعد أن أنجزت هذا البحث لايسعني إلا أن أشكر كل من وقف وراء هذا الانجاز بعد شكر رب العالمين

ويشرفني أن أتقدم بجزيل الشكر والعرفان الى أستاذي الفاضل الدكتور **جابر شنشول جمالي** الذي كان لرأيه السديد وعلمه الغزير وطيبة نفسه الاثر الكبير في أنجاز هذا البحث ولما أبداه لي من جهد في التوجية والارشاد والمتابعة فجزاءه الله عني خير جزاء

وأود التقدم بالشكر الى السيد رئيس القسم المحترم وكافة منتسبي القسم ممن كان له الفضل في أتمام هذا البحث

كما أوجه شكري وتقديري الى زملائي طلبة الدراسات العليا جميعا وكل من أنار دربي لأصل إلى هذه المرحلة

وأخيرا أقدم شكري وعرفاني الى من كانوا خير سند لي في تذليل العقبات , عائلتي

مروة فائق عبد الجبار

تأثير المؤثرات الميكانيكية على تحلل عوامل تقليل الاعاقة

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

من قبل
مروة فائق عبد الجبار
(بكالوريوس علوم في الهندسة الكيمياوية ٢٠٠٥)

جمادى الاخرة ١٤٢٩
حزيران ٢٠٠٨