EFFECT OF COMBINED ADDITIVES ON DEGRADATION RESISTANCE OF DILUTE POLYMER SOLUTIONS UNDER TURBULENT FLOW

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of Nahrain University in Partial Fulfillment
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Master of Science
in
Chemical Engineering
by
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B.Sc. in Chemical Engineering
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Certification

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Abstract

The experimental work was devoted to study the drag – reduction (DR) properties of various additive types, both in the single and binary mixed forms. Two polymer types, of high molecular weights 4 and 7 millions were used in the present investigation, namely, polyethylene oxide PEO as flexible synthetic polymer and Amylopectin as rigid polysaccharide from natural resources. Moreover, a certain type of natural Clay (Kaoline) and Aluminum sulfate (Alum) are included as suspended particles or in the colloid form. Sodium lauryl ether sulfate (SLES) as anionic surfactant was also used as additive. The drag reduction properties of the different additives were conducted in a closed loop circulation of turbulent water flow.

The flexible polymer, PEO at concentrations range from 20 to 100 ppm, was significantly high efficient drag reducing agent in turbulent water flow at 66810 Reynolds number. Otherwise, the time dependence DR showed that PEO undergo undesirable shear degradation under turbulent flow. Low concentrations enhance the degradation rate.

Alum could be considered as a good drag reducer agent. Otherwise Clay showed relatively low drag reduction ability. The drag reduction effectiveness of Clay as well as Alum additives is apparentable unchanged by shear re – circulation turbulent flow, up to 15 hours considered time. These may be to the stability of rod – like micelles in the suspended or colloid forms respectively.

Both SLES surfactant and Amylopectin rigid polymer showed moderate drag reduction effectiveness in turbulent water flow about 13.5% at 200 ppm concentration and 6.0 m^3/h flow rate. Moreover, Amylopectin was likely shear degradable, almost the same type of behavior was observed for Amylopectin as in the case of PEO.

The time dependence drag reduction with SLES additive explained an extraordinary behavior. The SLES surfactant with rod – like micelles remain relatively stable for certain time of turbulent recirculation according to the SLES concentration, after that the %DR decreases until minimum values were reached. Furthermore, micelles could be reformed during the stopping period leading to maximum drag reduction to be occurred.

A slight increase of drag reduction was observed by mixing Clay, Alum or Amylopectin with polyethylene oxide as Co – additives. While SLES – PEO admixture enhanced the DR performance. All of the considered Co – additives declined the susceptibility to degradation with shearing time recirculation flow. Increasing the concentration of Co – additive leaded to reduce the rate of degradation ability of admixture as drag reducer agent. SLES and Amylopectin Co – additive were slightly more efficient to decline the degradation ability.

The time dependence degradation behavior of the three solutions containing PEO + Clay, PEO + Alum and PEO + Amylopectin in turbulent flow was analyzed by modifying the fractional exponential decay equation $DR(t)/DR(0) = \exp[-(t/\lambda_f)^{1-nf}]$. The modified equation was found to fit the experimental data of the three solutions better than the original equation.

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Notations

Symbols	**Notations**	**Unit**
A	Area	m^2
C	Polymer concentration	ppm
D	Pipe diameter	m
%DR	Percent drag reduction	-
E	Energy necessary to break one bond	J/gmole
f	Fanning friction factor	
K	Constant in Eq.(4.1)	-
L	Test section length	m
Le	Entrance length	m
M	Molecular weight	g/gmole
M_∞	Limiting Molecular weight	g/gmole
N_A	Avogadro's number	6.0225×10^{-23} mol^{-1}
n	Constant in Eq.(4.1)	-
n_f	Fractional exponent in Eq.(2.6)	-
ΔP	Pressure drop	N/m^2
Q	Volumetric flow rate	m^3/h
R	Constant in Eq.(4.1)	-
Re	Reynolds number	-
T	Temperature	^0C
t	Time	h

u	Average velocity	m/s
$U_d(t)$	The energy originating from turbulence intensity that produces degradation	J
W	The average number of points per chain of polymer	-

Abbreviations

AAPE	Average Absolute Percentage Error
Alum	Aluminum sulfate
BPD	Barrel per day
CDR	Conoco Drag Reducer
CMC	Carboxymethylcellulose
DR	Drag Reduction
DRA	Drag Reduction Agent
DRE	Drag reduction efficiency
GG	Guar Gum
HEC	Hydroxyethyl Cellulose
MDR	Maximum Drag Reduction
PAM	Polyacrylamide
PAMH	Partially hydrolysed polyacrylamide
PCIP	Polycisisoprene
PDMS	Polydimethylsiloxane
PEO	Polyethylene oxide
PIB	Polyisobutylene
PMMA	Polymethylmethacrylate
ppm	Part per million
PS	Polystyrene
RDA	Rotating Disk Apparatus
SDS	Sodium Dodecyl Sulfate
SLES	Sodium Lauryl Ether Sulfate
TAPS	Trans Alaska Pipeline System

UV	Ultraviolet light
XG	Xanthan Gum

Greek Letters

ρ	Fluid density	kg/m^3
μ	Dynamic viscosity	Poise
λ	observed time scale of the relaxation	s

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Chapter One

1.1 Introduction

Energy is used usually for keeping the motion of a fluid over a solid surface and moving a solid body through a fluid. Unfortunately, a great amount of it is spent on overcoming drag, which results in loss and degradation of energy. 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 a drastic reduction of frictional resistance can be easily observed by injecting of minute amount of polymeric additives in a liquid flow [1]. In present of polymeric additive turbulent flow in a pipe thereby require a same volumetric flow rate and lower pressure drop [2].

The addition of small amounts of additives to the flowing fluids can show significant effects on a lot of flow types, including the stability of laminar flow, transition to turbulence, vortex formation and break – up [2]. Drag reduction by surfactants was reviewed by the work of Dodge and Metzner [3]. Surfactant solutions have become a favourite drag reducer owing to their chemical and mechanical stability that is an important requirement for practical applications [4].

The most effective drag-reducing polymers, in general, possess a linear flexible structure and very high molecular weight [5], such as Polyisobutylene, (PIB), and Polyethylene oxide, (PEO). The later is commercially available in a wide range of molecular weights, which is known to be suitable for use as a drag reducer. The dependence of drag reduction efficiency is known to be a function of polymer molecular weight, polymer concentration, pipe diameter and the degree of turbulence. Since solvent molecules take time usually to establish introductions with polymer molecules. Maximum drag reduction as function of time is obtained when the polymer solvent interaction reaches the state of homogeneity [6].

The drag reducing polymers are sensitive to flow induced shear degradation [7]. Degradation reduces the effectiveness of polymer additives because of the strong dependence of effectiveness on molecular weight [8]. Mechanical degradation is the process of rupture of the polymers into smaller molecules or break up of aggregates due to mechanical forces, which leads to a strong decrease of drag reduction [9].The additives demonstrated desirably high drag reduction efficiency while so undesirable mechanical degradation under turbulent flow occurs. Therefore, molecular degradation is one of the major defects in the drag reduction applications, 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 [10]. 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 [11].

1.2 Objectives of the Present Work

The current object of the present investigation is an attempt at gaining some experimental data in performance and mechanical degradation of Polyethylene oxide as drag – reducer in water flow using a laboratory circulation closed loop system. The study aimed also, to investigate the drag – reduction efficiency of some less known additives such as Amylopectin, Clay, Alum, and sodium lauryl ether sulfate surfactant with different concentrations by focusing mainly on their mechanical degradation kinetics as a function of time. Further aim of the experimental study was to investigate the effect of blending of Co – additives with the polyethylene oxide on its degradation behaviour.

Another objective of the present study is to modify the frictional exponential decay functions of admixtures, polyethylene oxide and other materials to examine their time dependent drag reduction efficiency, and with the ultimate goal of establishing a correlation between polymer degradation and the relative of polyethylene oxide in mixed solutions.

Chapter Two
Literature Survey

2.1 Phenomenon of Drag Reduction

The addition of a minute amount of polymer to a turbulent Newtonian fluid flow can result in a large reduction of the frictional drag in pipes and channels. This effect has been known in 1949 by Toms [12]. He was first discovered that addition of 10 weight parts per million of poly (methyl methacrylate) to monochlorobenzene undergoing turbulent tube flow resulted in substantial reduction in pressure drop at a given flow rate. This phenomenon has been the subject of intense, theoretical and experimental researches, since its discovery, due to its wide range of applications and from a fundamental fluid dynamics point of view as well.

Drag reduction additives can be classified in three categories, polymers, cationic – anionic – zwitterionic surfactants and suspended particles [13]. Among these, the most effective drag reducer is the high molecular weight polymers, but their high degradation rate decreases the effectiveness in the recirculation systems [14].

Over the past four decades, there was no universally accepted model that explains the mechanism by which macromolecules act to bring-about frictional reduction. However, it is commonly believed that drag reducing polymers additives interact with turbulent structure and suppresses turbulent eddies. Figure 2.1 shows the behavior of drag reduction agents before and after injection [15].

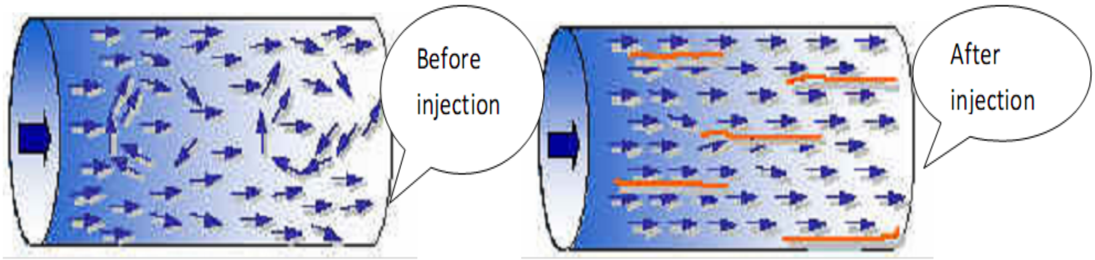

Figure 2.1 Drag Reduction Agent Effect [15]

Two principal theoretical concepts have been put forward to explain the phenomenon of drag reduction by polymers. The first can be attributed to Lumlely (1969, 1973) [16, 17], who proposed a mechanism based on the extension of the polymers. He postulated that stretching of randomly coild polymers, primarily in regions with strong deformations such as the buffer layer, which increases the effective (extensional) viscosity. Lumley also concluded 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.

Another theory was attributed by de Gennes in 1990 that drag reduction is caused by the elastic rather than the viscous properties of polymers [18]. This idea was supported by experiments showing that drag reduction also occurs when the polymers have been injected in the centre of the pipe [19]. Virk showed in 1975 that the quantity of polymer and its molecular weight were the factors with the largest influence on drag reduction for a given polymer and solvent [20].

Typically, larger quantities of polymer and higher molecular weight produce higher levels of drag reduction, until maximum drag reduction (MDR), as defined by virk et al. (1967) [21], is achieved. Furthermore, the quantity of polymer required to achieve (MDR) decreases with increasing Mw. The polymers with high molecular weight become more susceptible to degradation by chain scission, which effectively reduces the polymers ability to drag reduction [22].

2.2 Applications

The drag reduction effect is extremely interesting from a practical point of view. Liquids are mostly transported through pipes and a drag reduction, by adding a small amount of polymers, can offer large economic advantages and a larger effectiveness of this transportation. The first account of field trials was published by Bord, and Rossi in 1971[23]. They were concerned with the use of drag reducing additives in the pipeline transportation of waxy crude oil, and they found that there are no un expected side-effects of these additives that would militate against their commercial use. In 1971, Lescarboura et al. [24]. Presented a paper showing the use of high molecular weight hydrocarbon polymer called Conoco drag reducer CDR and polyisobutylene at different molecular weights in oil pipeline. 25% drag reduction was achieved with the use of CDR in 8in pipeline at 1000wppm concentration. In 1982, Burger et al. [9] published another field study on DR application at Trans Alaska Pipeline System. By using CDR as additive and in this application resulted in a significant capacity increase by (32,000) m^3/day. Another commercial application of CDR was in Kirkuk-Turkish pipeline through 1982-1987. An injection of 15wppm of CDR by nitrogen gas to the pipeline, about 3.7×10^5 BPD flow increment had been achieved [25].

Drag reduction by additives has been considered an effective way to reduce cost in closed – loop heating and cooling systems [26]. Also, in sewerage pipes and storm-water drains polymers have been used to increase the flow rates so that the peak loads do not result in over flowing; if only relatively infrequent use is required, this can be much cheaper than constructing new pipes [27].Turbulent drag-reduction has also an application in the firefighting. One of the first tested concepts for the application of polyethylene oxide, PEO for drag reduction was in pampers of New York Fire Department. The use of PEO decreased pumping power, increased throw and higher delivery rates. The polyethylene oxide also enhanced the coherence of the water jets [28].

Another application of drag-reducers is in hydraulic machines. The performance of centrifugal flow pumps could be increased by 5 to 10 percent using polyacrylamides at concentrations below 100ppm [28]. Polymers, such as polyethylene oxide and polyacrylamides have been tried in agriculture to increase water flow rates for irrigation purposes. In some instances a fertilizer has been combined with water. Of course, the environmental impact of the polymers on the crops needs to be ascertained [4]. Hydrotransport of solids, such as ash, coal, and sediments, by pipelines using drag reducing agents has been studied extensively. This application has a potential wide application because of the high tonnage of such solids at many locations worldwide [29].

2.3 Factors Affecting Drag Reduction

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 [6].

Percentage drag reduction increases as the concentration increases due to the increase in the number of available drag reducers. Further more, the drag reduction increased with polymer concentration for all the polymers until it reached a maximum, then it either decreased due to increase viscosity [30, 31] or leveled off depending upon the polymer species [31]. It is obvious that high polymer concentration yields higher drag reduction and that becomes more and more pronounced in highly turbulent flows [32].

Furthermore the effect of concentration on %DR is variable according to the nature of polymer. The flexible, synthetic polymers like polyethylene oxide and Polyacrylamide, cause maximum drag reduction (≅80%) in turbulent pipe flow at a concentration of few ppm. While, rigid polysaccharides, from natural resources, like Guar Gum (GG), Xanthan Gum (XG), Carboxymethyl Cellulose (CMC), require much higher concentration, i.e. ≥500 wppm to cause maximum drag reduction (≅60%) [33].

Effective polymeric drag - reduction additives are considered to be flexible, linear with a high molecular weight. The polymers with high molecular weight about a million g/mole are the more effective as a drag reducer [6].

Polymers with a molecular weight below 100000 seem 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 100 ppm .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[34].

The effect of molecular weight of Polyisobutylenes on effectiveness of drag reduction on gas oil was studied recently. Three polymers with different molecular weights ranging between 2.6 to about 6 million g/mole had been studied. It was found that friction factor decreases dramatically by increasing the molecular weight, which resulted in more increase of drag reduction [35].

It is well-known, that the drag-reduction phenomenon works in turbulent flow. Because increasing the fluid velocity means increasing the degree of turbulence inside the pipe, this will provide a better media to the drag reducer to be more effective. Therefore the degree of turbulence has a predominant effect on its effectiveness. But at high flow rate degradation may occur in drag reducer [25, 36, 37]. According to elastic theory, drag reducer doesn't stretch fully at high flow rate; this causes decrease in efficiency of drag reducer [38]. Berman and his Co-workers 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 reaches a constant level for a given solution and pipe diameters when no other limits are present. Moreover, these polymer threads have a high viscoelasticity and they may cause on interaction with turbulent eddies and consequently, a remarkable drag-reduction was observed [39, 40].

One of the most interesting factors in the study of the drag reducing fluid is the pipe diameter effects. It is well known that the drag reduction effectiveness of polymers increases with decreasing pipe diameter [33, 35]. Virk et al. concluded that the frictional drag reduction included by a given concentration of polymer increases with decreasing the pipe diameter [21]. Abdul Bari et al. had studied the effect of diameter for okra mucilage polymer (it is one of the natural polysaccharide polymer) in water and they concluded that the drag reduction increases by decreasing the pipe diameter; this means that the polymer will have a better media to work in smaller pipe [41].

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. Since a few amount of polymer solution, in part per million is added, many investigators have used this type of drag reducer for its high economics [42].

In a poor solvent the polymer molecule is attracted to another more than it is to solvent so that intermolecular contact might be more productive of entanglement than in a good solvent [43] . Polymer chains are more extended in good than in poor solvents [44].

2.4 Drag – Reducer Additives

2.4.1 Polymers

The most effective drag reducing polymers are essentially of linear structure, long chain, good solubility and high molecular weight. Drag reducer polymers are classified into two groups. Water - soluble polymers such as polyethylene oxide (PEO), polyacrylamide (PAM), sodium carboxymethyl cellulose (CMC), guar gum (GG), xanthan gum (XG), hydroxyethyl cellulose (HEC). The other group includes, hydrocarbon – soluble polymers such as polystyrene (PS), polyethylene oxide (PEO), polymathylmethacrylate (PMMA), polyisobutylene (PIB), polydimethylsiloxane (PDMS), and polycisisoprene (PCIP) [45].

Polyethylene oxide (PEO) has been the most widely studied for both laboratory and commercial application, such as fire fighting. Also, PEO have been used to increase the capacities of irrigation networks, and municipal sewer systems [46]. 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 [47]. 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 [48].

McComb, et al. [49] investigated the effect of polyethylene oxide (polyox grade WSR 301) (Mw = 4×10^6) on turbulence flow. It was found that the polymer additive reduced the turbulence intensity at a polymer concentration between 100ppm and 250ppm.

Furthermore, turbulent drag reduction with PEO in a Rotating Disk Apparatus (RDA) was investigated with different molecular weights. It was found that the DR efficiency of higher molecular weight is larger than that of lower molecular weight in a whole polymer concentration range up to 250 ppm as shown in figure 2.2 [6].

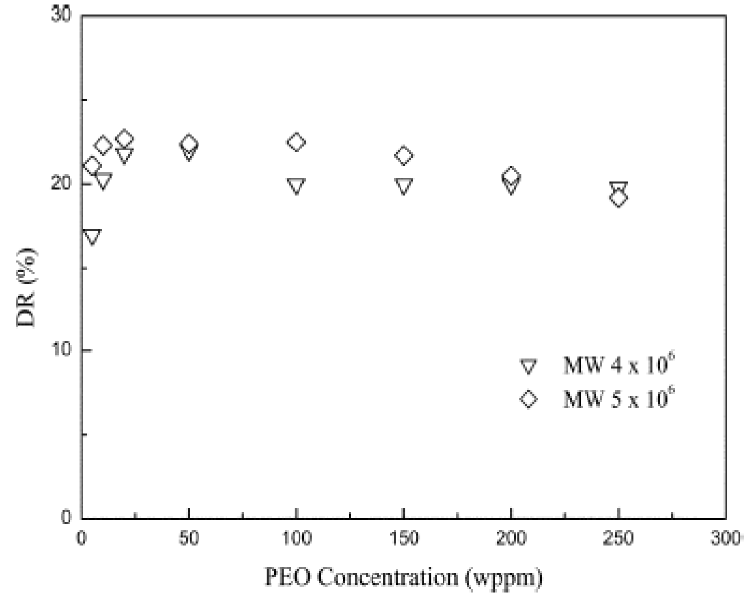

Figure 2.2 Drag reduction efficiency vs. PEO concentrations of two molecular weights [6]

Polyacrylamide (PAM) is the synthetic water soluble polymer and differs from PEO in that it has a side chain and is less susceptible to shear degradation. It was found that the polyacrylamids was the most effective one as drag reducing agent with maximum drag reduction percentage of 30% in concentration as low as 3 ppm by weight, when a wide variety of water–soluble polymers (poly ethylene oxide, poly acrylamide and guar gum) investigated [48].

Matthew et al. [50] investigated the relationship of turbulent drag reduction to molecular weight and molecular weight distribution for aqueous polyacrylamids solutions of concentration 200, 500 and 1000 ppm. Drag reduction experiments were carried out by circulating solutions in a rectangular flow channel having a flat wall and a wavy wall.

Yahya [51] investigated locally the drag reduction performance of PEO, PAM and XG. It was found that both flexible polymers, PEO and PAM are the more efficient as drag reducer additives. A maximum drag reduction of about 32% has been achieved when 100 ppm PEO or PAM were added at 6.0 m^3/h water flow rate.

Xanthan gum XG is a polysaccharide polymer. Sohn et al. [52] investigated the characteristics of polysaccharide xanthan gum as a drag reduction additive using rotating disk apparatus (RDA) with different molecular weight (2.8, 3.25, 3.41, and 3.61) $\times 10^6$ g/mol and concentrations up to 400 ppm. It was found that drag reduction increases with polymer concentration until a maximum drag reduction is reached, It was found also, that xanthan gum is confirmed to be a suitable drag – reduction agent in the case of relatively high – temperature and long – term applications.

Jaafer and Poole [53] studied the behavior of biopolymer xanthan gum as drag reducer in a circular pipe and an annular pipe, and found that xanthan gum is effective in both type configurations with the drag – reduction effectiveness of 40%.

Guar gum is used as a drag reduction additive with respect to the stability of its molecular structure at high shear forces. It is a plant polysaccharide with a semi rigid backbone. Xanthan gum and guar gum are the main shear stable drag reducers because of their rigid back bone molecular structure. The drag reduction efficiency of guar gum in deionized water by using a rotating disk apparatus has been examined and it has been found that guar is useful, water – soluble drag reducer, more resistant to the mechanical stress than the synthetic, water – soluble drag reducer, PEO [54].

Sodium carboxymethylcellulose (CMC) is a water soluble, colourless, odourless and non-toxic powder. The high molecular weight type is used as drag reducer agent with moderate effectiveness [55]. Pinho and Whitelaw used four concentrations (1000, 2000, 3000 and 4000 ppm) of Carboxymethylcellulose in pipe flow. They observed that MDR occurred at 2000 wppm CMC solution [56]. Emad [55] studied locally the drag reduction effectiveness, DRE of CMC and XG in tap water, river water and drainage water. It was found that the DRE of CMC is lower than XG. It was reported also, the DRE of any one can be improved by using there admixtures.

Polyisobutylene, is a flexible, linear and hydrocarbon soluble polymer. It is available in different high molecular weights. The turbulent drag reduction efficiency of polyisobutylene with three different molecular weights, 2.9×10^6, 4.1×10^6, and 5.9×10^6 was studied locally also in gas oil circulation system [57]. A gradual increase of drag reduction was achieved by increasing the polymer concentration and gas oil flow rate. Furthermore, the investigation showed that the degree of molecular weight is significantly in drag reduction performance. The highest molecular weight PIB shows the greatest degree of flow capacity increase. Different oil products were tested as solvents for the molecular weight PIB polymers. It was found that reformat was considered the best solvent for such polymers, which can be used as drag reducer agents [58].

The CDR drag – reduction additive is a polymerized straight – chain olefin monomer of one or more pure hydrocarbons above six carbon atoms [59]. CDR was used in Trans – Alaska crude oil and in Iraqi Turkish piplines to increase the flow rate [60, 55].

2.4.2 Surfactants

Drag reduction in turbulent pipe flow using surfactant additive was first reported by Mysels in 1948. He investigated the effect of aluminum disoaps on gasoline flow [61]. A solution of surfactant of enough concentration to form aggregates is called micelles, which are observed to cause drag reduction in turbulent liquid flow [61, 62]. A remarkable observation is that drag reduction approaching 80% can be realized when the composition as such that rode like micelles are formed [63]. Several types of surfactants which include certain anionic, cationic, nonionic and zwitterionic are considered as powerful drag reducers in turbulent flow in pipes and can hence contribute to significant energy savings [61].

There are three mechanisms for surfactant drag reduction; all of them revolve around dampening turbulence eddy currents and cross – directional flow, which in turn dissipate energy loss. The first theory is that the rod – like micelles become entangled and their elastic properties hinder cross – flow [64].

The second theory is that the micellar structure leads to an increased extensional viscosity which is responsible for the dampened eddy effects [29]. The third theory is that the rod – like micelles become elongated in the direction of the flow and lead to a thickening of the viscous sub layer of flow. This thickened sub layer then opposes the cross – directional flow and eddy currents [65]. The common surfactants as drag reducer are the quaternary ammonium salt cationic surfactants, such as cethyltrimethyl ammonium chloride and stearyltrimethyl ammonium chloride. Sodium salicylate is usually added as counter – ion [66]. The addition of a quaternary ammonium salt cationic surfactant was effective in reducing both drag and heat transfer in a turbulent pipe flow [26, 67].

2.4.3 Suspended Particles

The study of drag reduction caused by the addition of suspended solid matter was initiated by the fact that turbid streams of water were found to flow faster than clear ones [29]. The suspended matter such as clay, sand and similar materials generally exhibit strongly passive method of drag reduction [68]. The drag reduction achieved for carboxymethylcellulose in raw water (river water) is higher than in tap water, due to the turbidity of the former [55]. It is possible that the presence of clay particles in water influence the viscosity of flowing water, therefore, the increasing in the drag reduction effectiveness in exciting of clay is consistent with the observed changes in solution viscosity [55, 68]. Clay solid particles were found to behave as efficient drag – reducing agent. A gradual increase of drag – reduction and throughput was achieved by increasing the clay concentration and water flow rate and decreasing the pipe diameters. The drag – reduction ability of carboxymethyl cellulose was improved noticeably by mixing with clay as combined additive [69]. Although solid particles have not been studied as thoroughly as polymers and surfactants, there are nevertheless two important factors when they are put to industrial use it is easy to add solid particles to the flow medium and then withdraw them again later. They are also not prone to mechanical degradation. However, the degree of effectiveness achieved, in comparison to polymers and surfactants, is not so great [70]. A certain type of local natural clay (Kaolin) was tested as suspended particle additive up to 500 ppm in water flow. It was found that clay additive concentration above 250 ppm and water flow rate 5-6 m^3/h are suitable conditions to get expected drag – reduction effectiveness [51].

2.5 Degradation of polymeric additives

2.5.1 Introduction

Degradation hampers the practical usage of polymers for turbulent drag reduction application. Degradation is a deleterious process, to degrade a substance is to impair it in respect to some physical property or to reduce its complexity, in which the activation energy of polymer chain scission is exceeded by the mechanical action on the polymer chain, thus bond rupture occurs. In turbulent flow, molecules undergo scission when fully extended; decreasing the polymer chains molecular weight. As previously described, the molecular weight of a polymer is a large factor in determining its drag reduction efficiency. Scission of molecules therefore decreases their ability to reduce the wall shear stress [71].

Effective polymeric drag reduction additives are considered to be, flexible, linear with high molecular weight, above four millions g/mole. The polymer additives undergo usually undesirable mechanical and chemical degradation under turbulent flow and rotation speed. This leads to decrease the drag reduction efficiency by increasing the time of flow [57].

Polymers degrade by several different mechanisms, depending on their inherent chemical structure and on the environmental conditions to which they are subjected. A degradation result from an irreversible change in the material which eventually leads to its breakdown i.e. looses in molecular weight and then, losses its effectiveness. There are five major mechanisms of polymer degradation: mechanical, thermal, radiation induced, photo and oxidative [72].

2.5.2 Mechanical Effects

Mechanical degradation is a process of rupture of the polymers, which leads to a strong reduction in molecular weight [73]. Therefore, polymeric degradation has become of the critical issues in applications dealing with polymer induced turbulent drag reduction [74]. Superfloc A110 (partially hydrolysed polyacrylamide) (PAMH), subjected to mechanical degradation in re – circulatory system when it is used as drag reducer. At the start the drag reduction is quite high, after an initial fast decay, the degradation slows down as shown in figure 2.3 [75].

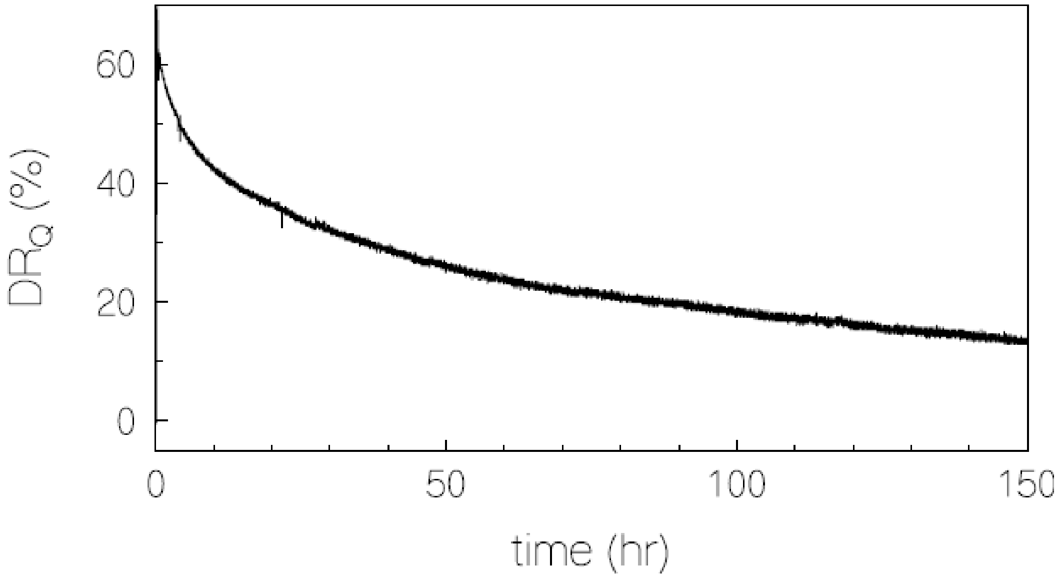

Figure 2.3 Typical degradation curve of superfloc A110 solution at constant flow rate Q = 2850 l/hr [75]

Polymers are continuously subjected to deformation, especially in the pump, which cause the scission of the polymers and this might dramatically occurs when the re-circulation system was used experimental set-up. 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 rotary pumps, especially the type of external gear pump, reduces the polymer degradation. In the external gear pump, intermeshing gears rotate with close clearance inside the casing. Thus, the effectiveness of high molecular weight polymer as a drag reducer lasts for a longer time by using Gear pumps [76].

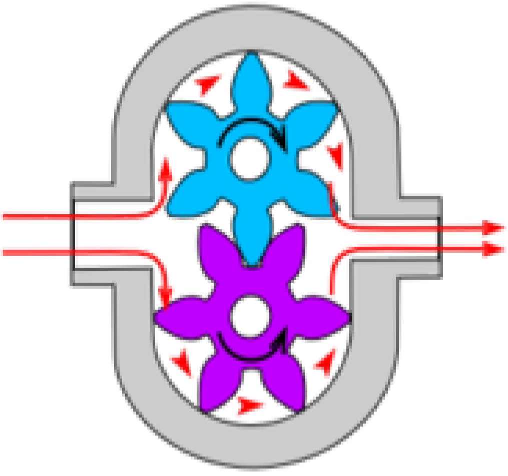

Figure 2.4 Gear Pump [76]

Munstedt [77], studied pipes configuration varies from straight line to inclined line and/or right angle and others. The best shape to reduce the degradation of high molecular weight polymer is the straight line shape. Therefore the pipeline operating system prefers this shape through the pipelining, unless the geography of the area obliges them to use other shapes. Figure 2.5 illustrates the effectiveness of mechanical configuration on drag reduction.

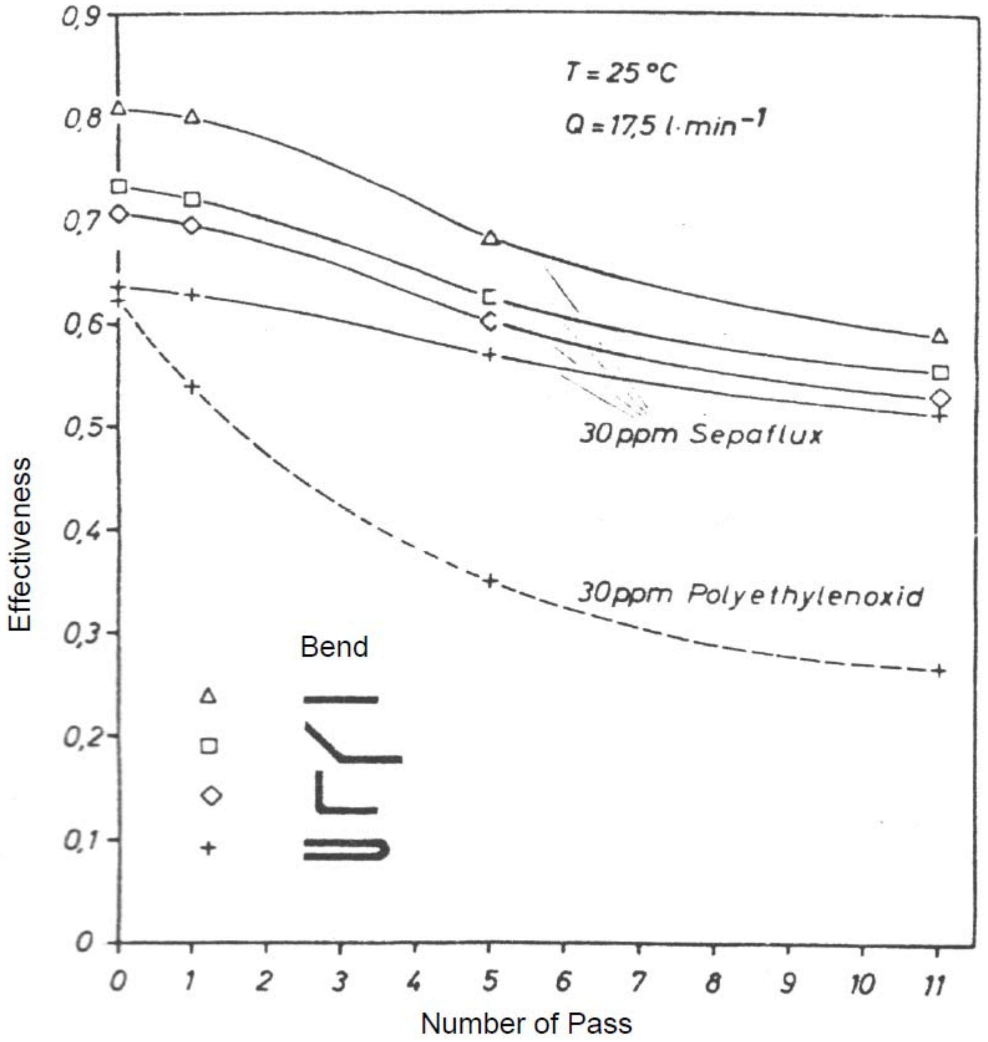

Figure 2.5 Effect of mechanical configuration on polymer effectiveness [77]

Losses in any pipe flow system occur when irregularities exist in the flow path; examples of irregularities that incur losses are expansions, contractions, valves, bends, and any sort of obstruction [78]. Degradation of polymer solutions occurs when the fluid stresses that is developed, during deformation and/or flow, becomes large enough to break the molecular chains. The shear degradation depends on the structure of the molecule, molecular weight, and solution concentration [79].

2.5.3 Thermal and Radiation Effects

Thermal degradation represents the point where the chemical bonds of the polymer acquire enough thermal energy to break or rearrange spontaneously at significant rates. Thermal degradation plays an important part in determining processibility [80]. It is generally involved changes to the molecular weight, molecular weight distribution and color [81]**.** 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 [34]. The degradation of drag reduction in polymer solutions is dramatically affected at high temperature as shown in figure 2.6 [82].

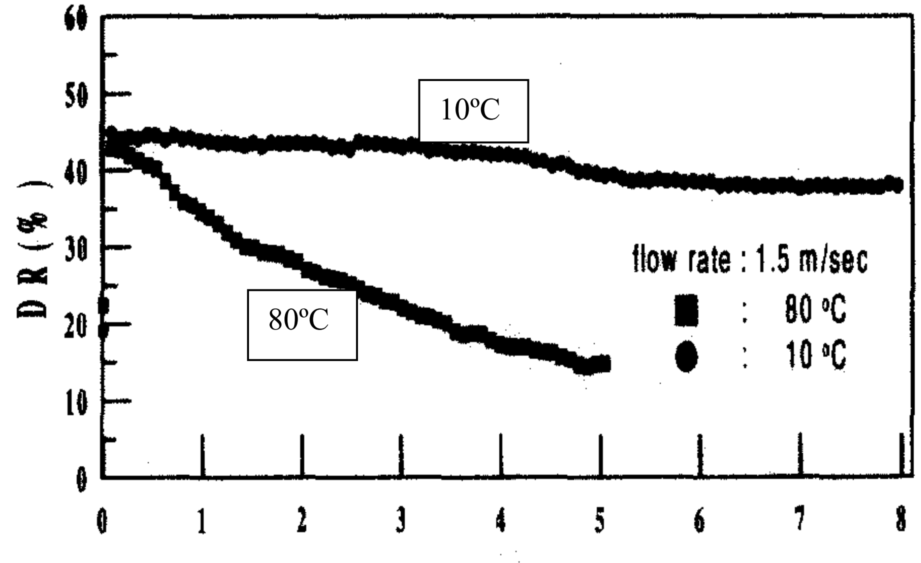

Figure (2.6) Degradation of drag reduction effect at different temperatures for 100 ppm copolymer solution [82]

Degradation of photodegradable molecule is caused by the absorption of photons particularly those wavelengths found in sunlight, such as infrared radiation, 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 in to small pieces by photons [83].

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 [84].

2.5.4 Chemical Effects

Chemical degradation of polymers involves a change of the polymer properties due to a chemical reaction with the chemical agents such as oxygen, ozone or acids [34, 85]. There are many different types of possible chemical reactions causing degradation however most of these reactions result in the breaking of double bonds within the polymer structure, so the result of chemical degradation can be to break up the long polymeric chains, a process known as depolymerisation [86].

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 varies from polymer to polymer. Most researches on this subject have been directed towards the oxidation of hydrocarbon polymers. There are differences in mechanism between the oxidation processes of saturated and unsaturated hydrocarbons [84].

2.6 Summarized Researches on Degradation

Gadd [87] 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 in addition to guar gum solution with concentration not more than 60 ppm. 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. [88] 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.

Patterson and Abernathy [22] studied the importance of the entrance effects on degradation in turbulent flow by using polyethylene oxide (PEO) solutions. They observed that the 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.

Nakano and Minoura [44] observed that the rate of scission of polymer chains becomes greater in a good solvent than in a poor solvent at low concentration by noting that the interaction between polymer molecules weakens at low concentrations.

Horn and Merrill [11] showed that polymer chains tend to undergo scission at the midpoint where stresses are the highest, which has the effect of halving the molecular weight for each chain scission event that occurs. It has been shown that as the chain length is increased (i.e. molecular weight is increased for a given polymer), the polymers become more susceptible to degradation by chain scission, which effectively reduces the molecular weight and the polymers ability to reduce drag.

Tabata et al. [89] measured changes in the number average molecular weight induced by high speed stirring in a benzene solution of poly (methyl methacrylate) (PMMA). They found that at lower concentrations of polymer solution the molecular weight decreased faster, which is consistent with the fact that at a lower concentration of polymer solution the number – average molecular weight decreases more rapidly. It was also observed that the main chains of (PMMA) were ruptured by the high speed stirring.

Yang et al. [90] studied mechanical and thermal degradation of poly ethylene oxide and polyacrylamide in rotating disk apparatus. They found that polymer degradation due to high shear force the process of drag reduction is found to be more apparent at lower polymer concentrations. Furthermore, they made tests on thermal effect and showed that polyacrylamide is more thermally stable than poly ethylene oxide.

Nijs [91] has mentioned without supporting any experimental evidence that drag reduction agent performance can be affected at high shear force regions in pipeline such as partially opened bends and valves. Drag reducing agents are sensitive to shear forces produced by pumps. DRA's do not survive shear stresses raised by centrifugal pumps and appears to be badly degraded going through positive displacement pumps.

Myska and Zakin [92] reported that the polymer solution degrade irreversibly and lose their drag reduction behavior under shear forces. And cationic surfactants degrade rather under high shear, but the structures were repairable through regaining drag reducing abilities when shear was reduced.

Several correlations between DR efficiency and mechanical degradation were published [93-95]. Brostow and coworkers have developed a model from a statistical mechanical approach [94] and have investigated the validity of their model based on computer simulations. The drag reduction efficiency and mechanical degradation were related to macromolecular conformation in solution. The DR efficiency is proportional to the molecular weight of the polymers, as given in equation 2.1 [95].

$$DR(t)/DR(0) = M(t)/M(0) \qquad \ldots (2.1)$$

Where

DR (t); percent drag reduction at time t

DR(0); percent drag reduction at time 0

M (t); effective number-average molecular mass at time t

M (0); effective number-average molecular mass at time 0

More mechanical degradation was observed in a poor solvent than in a good solvent under the same flow conditions [93, 44]. A limiting molecular weight can be defined by $M_\infty \equiv \lim_{t\to\infty} M(t)$. M_∞ becomes smaller in the poor solvent than in good solvents for a given polymer. Brostow et al. [93, 94] noted that the points on the chain where change of direction occurs 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. The average number of points per chain of the latter kind is denoted by W, and

$$M_\infty = \frac{M_0}{1+W} \qquad \text{… (2.2)}$$

Here, *W* is proportional to the number of breakable sequences having two different orientations and changing extended-to-compact or compact-to-extended conformations. For a polymeric drag reducing agent, *W* can also be related to the drag reducer concentration C, the energy $U_d(t)$ originating from turbulence intensity that produces degradation, and the energy *E* necessary to break one bond [94].

$$W = \frac{M_0 U_d(\infty)}{C N_A E} \qquad \text{... (2.3)}$$

Where N_A is Avogadro’s number.

By introducing the single exponential model (with h as the decay constant), the following relationship could be obtained: [94]

$$DR(t)/DR(0) = 1/(1+W(1-e^{-ht})) \qquad \text{… (2.4)}$$

A large value of h indicates fast degradation, and a large value of W implies a low shear-stability. Kim [96] adopted the theoretical model for molecular degradation proposed by Brostow et al. [94] to their experimental data and obtained an excellent fit by using equation 2.4, for monodesperse polystyrene polymer.

A single-relaxation decay model was adopted to explain a time-dependent relative drag reduction efficiency which is related to mechanical degradation as given in equation 2.5. The empirical equation associated with a slow relaxation time of the polymer solution [97, 98].

$$DR(t)/DR(0) = \exp(-t/\lambda_s) \quad \ldots (2.5)$$

The $1/\lambda_s$ quantifies the loss rate of drag reduction activity or the rate of degradation. Despite the successful applicability for this single exponential decay model for shear resistant drag reducers especially in describing short time degradation behavior, it is not difficult to conjecture the inadequacy of this model.

Choi et al. [6] has investigated the drag reduction efficiency by dilute aqueous solutions of polyethylene oxide with two molecular weights in a rotating disk system (RDS) and found that equation 2.5 does not fit the experimental data relatively well. Therefore, to improve the fitting, a fractional exponential form, often called the Kohlrausch, William, and Watt (KWW) function, has been modified from the single exponential decay function as shown in equation 2.6. This equation has been used to describe the second order nonlinear relaxation behavior.

$$DR(t)/DR(0) = \exp [-(t/\lambda_f)^{1-nf}] \qquad \ldots (2.6)$$

λ_F, is an observed time scale of the relaxation process and n is a functional exponent. The degree of non-exponentially considers the breadth of the distribution of relaxation time. Choi, [6] applied equation 2.6 and had shown that the relative drag reduction effectiveness was fitted better with equation (2.6) than equation (2.5).

Kim et.al [96] investigated the degradation of high molecular weight polystyrene under turbulent flow using a rotating disk apparatus for benzene, chloroform and toluene solvents at 150 ppm polymer concentration. 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.

Sohn et al. [52] investigated the degradation of polysaccharide xanthan gum in an aqueous solution by using rotating disk apparatus, they found that polymer degradation occur due to high shear forces and increase with turbulence intensity. Xanthan gum behaves as a more shear – stable drag – reduction agent in the deionized water, as well as in the salt solution, than the most flexible synthetic polymers.

Lim et al. [99, 100] investigated turbulent drag reduction induced by polyisobutylene molecules dissolved in kerosene and their chain degradation under a turbulent flow, using a rotating disk apparatus. It was found that the drag reduction efficiency decreases with time due to mechanical degradation of the polyisobutylene, as shown in figure 2.7 [99].

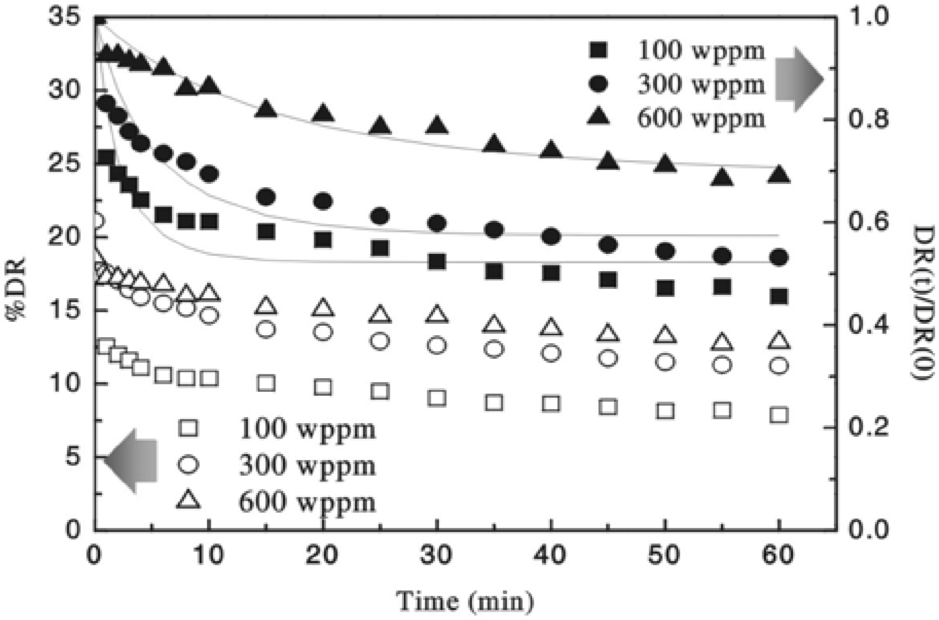

Figure 2-7 Percent and relative drag reduction efficiency vs. time for three different concentrations of PIB L-120 at 1800 rpm [99].

Choi et al. [6] 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 concentration.

Shanshool et al. [101] investigated experimentally the mechanical, shear degradation of polyisobutylenes, with high molecular weights of 2.5, 4.1 and 5.9 million g/mole by exposing there dilute solutions in kerosene to high mechanical stirring. It was observed that the susceptibility of polyisobutylene to degradation increases with increasing the polymer molecular weight, concentrations, stirring speed and exposed time. The behavior of molecular degradation during the drag reduction experiments were in agreement with the observation for shear degradation by stirring.

Atshan [102] studied the performance of two water – soluble polymers, polyacrylamide and xanthan gum as drag reducers in pipe flow; it was found that polyacrylamide and xanthan gum additive undergo undesirable mechanical degradation with increasing of circulation time, leading to lower drag-reduction performance. The results showed also that the DRE in vertical piping were significantly lower than in straight types for both additives.

Elbing [103] studied the degradation of polyethylene oxide and polyacrylamide in turbulent pipe flow in pure water and sea water as a solvent. He found that the results obtained with PEO and PAAM polymer solutions support the prediction made by the universal scaling law for polymer chain scission by vanapalli et al. in 2006 that the maximum drag force on the chain is proportional to $Re^{3/2}$. It was observed also, that salt water has minimal impact on the degradation process relative to solutions prepared with a pure water solvent.

2.7 Degradation with Co – additives

Non – polymer molecules are much less susceptible to degradation than polymers. They are also substantially less effective drag reducing agents [104 – 106]. The combinations of polymer and non – polymer molecules behave synergistically in turbulent flow, and can be used to achieve both greater levels of drag reduction and lower susceptibility to degradation than polymers alone [105]. This process is commonly used to enhance the ductility and toughness of brittle homopolymers or increase the stiffness of rubbery polymers. The basic properties of polymers may be enhanced by physical as well as chemical means. Useful polymers contain small quantities of additives to aid processing and increase the resistance to degradation. The physical properties of the base polymer may be modified by the presence of such additives [107].

Kim et al. investigated whether mechanical and thermal degradation could be effectively avoided by adding sodium dodecyl sulfate, SDS surfactant to the polymeric solution such as PEO, PAAM, and XG, thereby enhancing the bonding forces between the polymer molecules. It was observed also, that the admixture of polymer and SDS surfactant would appear to be more effective in preventing the effect of degradation at high temperatures than at low temperatures. However the degradation effect can maintain at a minimum in both low temperature and high temperature systems [82]. It was found elsewhere, that the present of SDS Co-additive in polymeric solutions has the characteristics of suppressing shear degradation [108].

Rho et al. [11] investigated the mechanical degradation of polyacrylamide in turbulent aqueous flow in district heating systems. It was found that the degradation is suppressed by adding sodium sulfite, as Co – additive.

Brostow and Lobland [109] studied the mechanical degradation of homopolymer polyacrylamide and graft copolymer polyacrylamide with Amylopectin. It was found that the grafted polymer has resulted in significantly slower mechanical degradation in flow compared with the respective homopolymer as shown in figure 2.8.

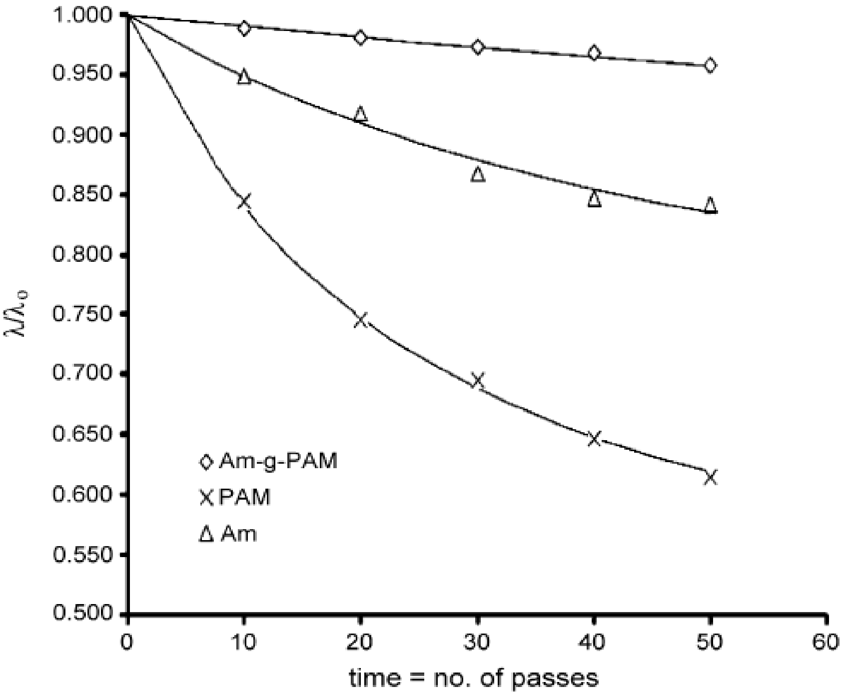

Figure 2.8 Relative drag reduction (λ/λ_0) for aqueous solutions of grafted copolymer and homopolymer as a function of time for 500 ppm concentration of each drag reducer

CHAPTER THREE
Experimental work

3.1 Materials

Polyethylene oxide with a molecular weight of 7×10^6 g/mole was acquired from OMA Company for Chemical Compounds. Amylopectin which is a branched polysaccharide was acquired from FLUKA Company, Germany.

Iraqi natural Clay of a high purity (Kaolin) and Aluminum sulfate (Alum) were brought from local market. Alum is used usually for water treatment to remove suspended slurries. The analysis of Clay was done in laboratory of ministry of Industry and Minerals, Baghdad.

The average results are shown in Table 3.1

Table 3.1 composition of clay

Compound	wt %
SiO_2	46
Al_2O_3	11.89
CaO	9.10
MgO	7.20
K_2O	2.26
Na_2O	1.09
L.O.I.	14.80
Others	7.66

L.O.I: loses on ignition

Sodium lauryl ether sulfate SLES is an anionic surfactant [$R(OCH_2CH_2)_n OSO_3 Na$], made from alcohol ether sulfated with chlorosulfonic acid or SO_3, and then neutralized with sodium hydroxide [110]. SLES has a good solubility in water and excellent foaming and thickening performance [111]. Sodium Lauryl Ether Sulfate (SLES) with molecular weight 372 g/mole was acquired from General Company of Vegetable Oil Industry.

The tap water was used as flowing fluid, for all drag reduction experiments.

3.2 Preparations of additives solutions

The polyethylene oxide and Amylopectin solutions were prepared by making the concentration of additives 2% by weight in water in separate conical flask. Thus 4 g of polyethylene oxide additive is mixed with 200 ml tap water and 5g of Amylopectin additive is mixed with 250 ml tap water at laboratory temperature. The container was placed in shaker, type KOTTERMANN 4040, GERMANY, with 100 rpm as shown in figure 3.1.The shaking was done for 1 hour for the amylopectin and about 25 hours for PEO, to reach homogenous solutions. The solution was diluted to 1% and placed in dark container to avoid photo degradation and allowed to standing for 24 hours at room temperature prior to its uses. The shaker was used instead of mechanical stirrer to avoid any polymer degradation; hence it has no sharp edge that could expose to high shear force.

Figures 3.2 and 3.3 show the behavior of Polyethylene oxide and Amylopectin in water respectively after a shaking time of about one hour. These figures show clearly that Amylopectin was dissolved completely after one hour, while the main portion of polyethylene oxide is still undissolved.

Figure 3.1 Electrical Shaker

Figure 3.2 polyethylene oxide in water after 1 hour

Figure 3.3 Amylopectin in water after 1 hour

Sodium lauryl ether sulfate additive was dissolved immediately by taking 10g SLES in 500ml water to get 2% wt concentration. A homogeneous solution was observed by mixing in the shaker for about 15 minutes.

Clay and Alum have been crushed carefully by a hammer and the required amounts were suspended in 500 ml water.

3.3 Flow loop

The performance of the drag reducing additives was evaluated in a laboratory scale circulation loop [30]. It consists of reservoir tank, pipes, valves, gear pump, flow-meter and manometer. The apparatus will be used to investigate the polymer degradation in turbulent pipe flow as function of time. The schematic diagram of experimental set up is shown in figures 3.4 and 3.5.

The reservoir tank with dimensions 0.7×0.7×1 m made of galvanized metal was used as feed tank. The reservoir tank was supported with galvanized steel pipes of inside diameter, 0.0508 m to perform the flow measurements. A gear pump of 0.0508 m diameters, 1440 rpm and total head of 6m was used to deliver the fluid at high turbulence. Gear pump was used to avoid additive mechanical degradation.

Piping starts from the reservoir tank through the pump, reaching a connection that splits it into sections as shown in figure 3.4. The first section returns back to the tank using 0.0508 m pipe as by pass while the other with 0.03175 m pipe diameter for testing purposes.

The test section of 2m long was placed away from the entrance length. The minimum entrance length required for a fully developed flow profile was calculated from the relationship suggested by Desissler, as given in equation 3.1 [112].

$$Le = 50\ D \qquad \ldots (3.1)$$

Where,
Le = entrance length, m
D = pipe inside diameter, m

Therefore, the minimum entrance length for the used pipe of 0.03175m inside diameter is,

$$Le = 50 \times 0.03175 = 1.5875\ m$$

The water flow rate was measured with a float flow meter of 0.0508 m diameters and flow indicating range (0.6-6) m^3/h. Figure 3.6 shows the calibration of the flow meter. A U-tube manometer filled with distilled water was used to evaluate the pressure measurements in mm H_2O. The experiments were performed in temperature range from 23 to 28 C.

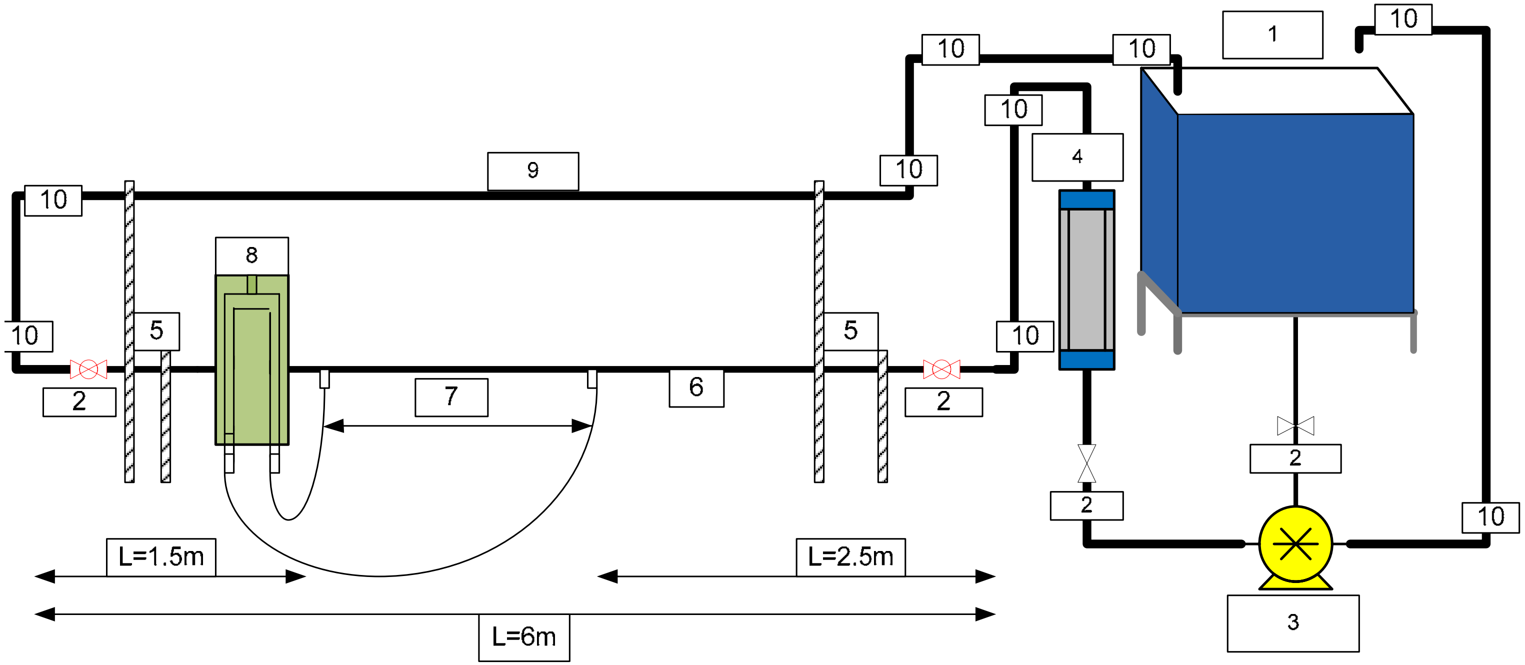

Figure 3.4 Schematic Diagram of Experimental Rig

1. Tank (0.49m)
2. Valve
3. Gear pump
4. Flow meter
5. Stands
6. 0.03175 m Pipe
7. Test Section (L=2m)
8. Manometer
9. 0.0508 m Returned Pipe
10. Elbow 90º

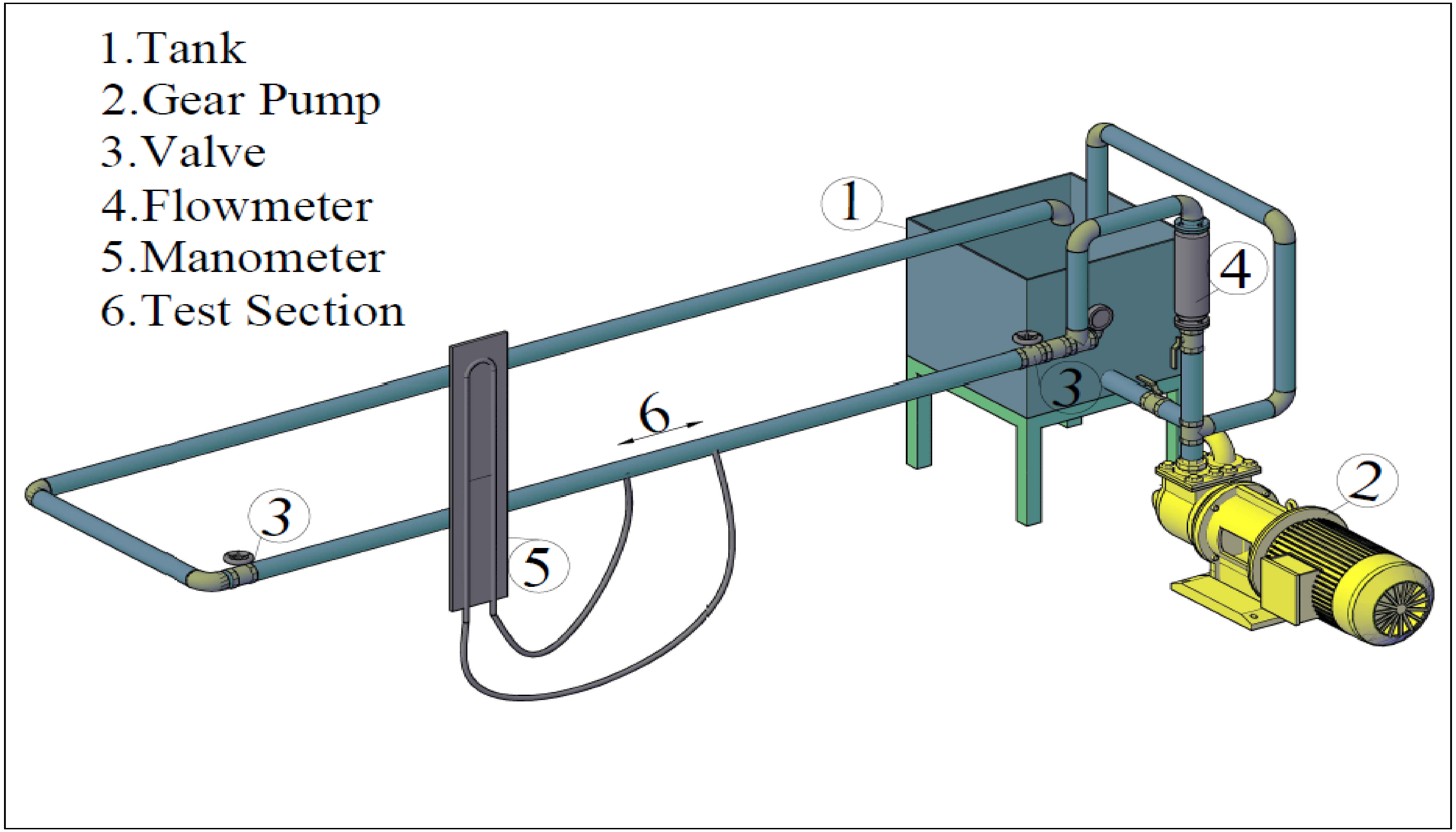

Figure 3.5 Experimental Rig Showing Closed Loop Circulation System

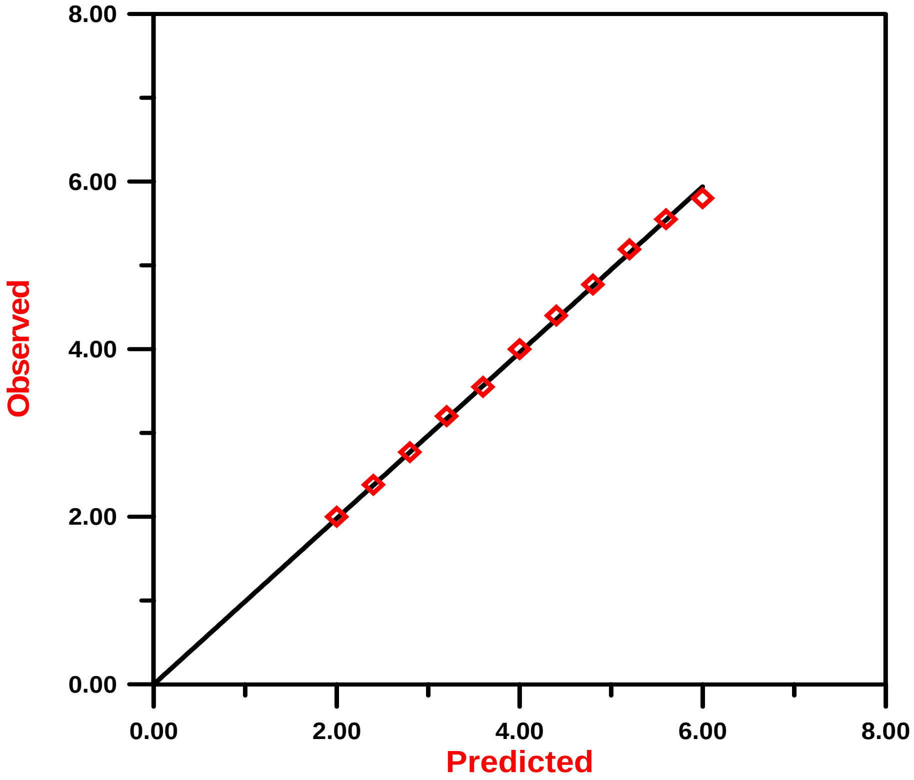

Figure 3.6 Calibration of flow meter for water flow rate in m^3/h

3.4 Experimental Procedure:

At start an experiment, the reservoir was filled with about 100 liters water. After operating the pump the fluid is allowed to flow through only one of the three pipe sizes by closing the other valves. Then connect each tube end of the pressure taps in the upstream and down stream with U- tube manometer, and allow the bubbles in the connecting viny1 tubes to flow away, to avoid any error in the reading. Then open the by- pass valve and closed pipe valve to check the manometer so when the level of the water in manometer is the same level that indicate the reading is correct.

The required additive concentrations were prepared in one liter water and mixed for about 15 min. The solution flow rate is fixed at the certain value (6m^3/h) by controlling it from the bypass section. Pressure drop readings are taken to this flow rate in (mm H_2O) at different time for the same additive and concentration. The same procedure is repeated in order to obtain more data at various concentrations of additives and different time.

For degradation experiments purposes, the same steps mentioned above were done and manometer reading was taken every one hour until the effectiveness of additive became noticeable. For the degradation experiments at longer circulation time (more than seven hour), the operation of flow loop was stopped at the end of working day and then repeated in the next day until reaching the required operation time.

3.5 Experimental calculations

The weight of polymer required to prepare (X) ppm in 100 liter water is obtained from the following equation

$$Weight = \frac{\rho_{water} \times 100 \times X}{10^6} \qquad \text{... (3.2)}$$

Where ρ_{water} = density of water in g/l

For example to obtain 50 ppm:

Weight = $\frac{1000 \times 100 \times 50}{10^6}$ = 5.0 g additive required for 100 liter solution

For 2 % polymer solution

$$= \frac{5 \times 100}{2} = 250 \text{ g solution needed}$$

Pressure drop readings through testing section before and after drag reducer addition, were needed to calculate the percentage drag reduction %DR as follows [10].

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

Where: $\Delta P_{untreated}$ = pressure drop without drag reducer addition

$\Delta P_{treated}$ = pressure drop with drag reducer addition

In current study the percentage decrease in drag reduction efficiency was calculated from the following equation.

$$\%Decrease = \frac{DR(0) - DR(t)}{DR(0)} \qquad \ldots (3.4)$$

Where:

DR(0) and DR(t) are drag reduction at time zero (beginning) and time = t respectively.

Friction factor in term of fanning friction factor can be calculated as follows [113].

$$f = \frac{D \times \Delta P}{2 \times \rho \upsilon^{2} \times L} \qquad \text{... (3.5)}$$

f= fanning frication factor

D = pipe inside diameter, m

L = distance between the pressure taps, m

ρ= density of solution, g / l.

ΔP = pressure drop, mm H_2O.

Chapter Five

Conclusions and Recommendations

5.1 Conclusions

1. The flexible, linear with a high molecular weight polyethylene oxide is significantly more efficient drag reducing agent in turbulent pipe flow than Amylopectin as rigid, branched polymer of polysaccharide types, Clay, Alum, as suspended particles or colloid and SLES surfactant.

2. Percent drag reduction for all considered additives were found to increase by increasing the agent concentration. This behavior was different according the type of additive. The PEO polymer achieves the highest %DR than other additives and it is equal to 31% at 100 ppm concentration and 6.0 m^3/h flow rate, while SLES and Amylopectin have moderate %DR equal to 13.5% at 200 ppm concentration and 6.0 m^3/h flow rate. Otherwise the %DR of Clay and Alum equal to 10.5% and 18% respectively at 300 ppm concentration and 6.0 m^3/h.

3. The drag reduction effectiveness of PEO additive can be slightly improved by combined mixing with Clay, Alum, SLES or Amylopectin.

4. A gradual decrease of percentage drag – reduction was observed for PEO and Amylopectin as circulation time progresses, due to mechanical degradation of polymer molecules. Alum and Clay additives were found

not to degrade under turbulent water flow as circulation time progresses, up to 15 hours.

5. The percentage drag reduction for the SLES surfactant alone was found fixed at the first time but after some hours a gradual decrease of percentage drag – reduction was observed, due to mechanical degradation.

6. The present of the Co – additive in small amounts with PEO in turbulent water flow acts generally as inhibitor for degradation behavior of the admixture additives, due to the molecular interaction and to the degradation stability of some Co – additives as in case of Clay and Alum.

7. The time needed to reach maximum drag reduction with SLES – PEO admixture was taken as indication to reach maximum micellization of surfactant with PEO. This time was increased as SLES concentration increases. The degradation rate with PEO – SLES admixture was noticeably decreased, mainly at high SLES concentrations, i.e. 200 ppm.

8. A correlation between polymer degradation and the weight ratio of PEO to the second material in the admixture was established, by modifying the fractional decay for PEO + Clay, PEO + Alum and PEO + Amylopectin solutions. The modified equation fits experimental data better than KWW decay function.

5.2 Recommendations

1. Studying, other flexible synthetic polymers, such as polyacrylamide and polyisobutylene on shear degradation behavior in presence of Co – additives.

2. Further work can be carried out to investigate the micellization rate of different surfactant types and there behavior against shear degradation.

3. Studying the effect of salt on binding of polymer and non – polymer additives in solution and also the effect of such aggregation on the degradation of polymer.

4. Studying the effect of increasing the temperature on the degradation of polymers such as PEO and on the admixture of polymer with other agents such as PEO with XG.

5. More accurate correlations to predicate the drag reduction behavior of single additives and Co – additives. More attention would be taken to their degradation.

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Appendices
Appendix A

Drag Reduction Effectiveness with Different Additives

Table (A-1) Experimental Results for PEO as Drag Reducer in Water at different flow rates in 0.03175 m pipe diameter

Flow rate (m^3/h)	**Concentration (ppm)**	**Re**	**%DR**	***f***
2	20	22270	4.5	0.004379
	40	22270	5	0.004356
	60	22270	6.5	0.004288
	100	22270	7.5	0.004242
4	20	44540	6.5	0.004288
	40	44540	8	0.004219
	60	44540	12.5	0.004012
	100	44540	17	0.003806
6	20	66810	10	0.004127
	40	66810	19.5	0.003691
	60	66810	24	0.003485
	100	66810	31	0.003164

Table (A-2) Experimental Results for Clay, Alum, SLES, and Amylopectin as Drag reducer additives in Water at flow rate 6.0m^3/h in 0.03175m pipe diameter

Materials	Concentration (ppm)	%DR
Clay	50	5
	100	5.5
	200	9.5
	300	10.5
Alum	50	11
	100	14.5
	200	16.5
	300	18
SLES	50	10.5
	100	11.7
	150	12.8
	200	13.5
	250	12.5

Table (A-2) continue

Amylopectin	50	8.7
	100	9.8
	150	11.2
	200	13.6
	250	12

Appendix B

Time Dependence of DR Effectiveness with Different Additives

Table (B-1) Effect of mechanical degradation on drag reduction effectiveness of PEO solution at 20 ppm concentration and 6m^3/h flow rate

Time (h)	**%DR**	***f***	**%Decrease**
0	10	0.004127006	0
1	7.6	0.00423706	24
2	6.2	0.004301258	38
3	5.1	0.004351699	49
4	5	0.004356285	50
5	4.6	0.004374627	54
6	4	0.00440214	60
7	3.6	0.004420482	64
8	3.3	0.004434239	67
9	3.3	0.004434239	67
10	2.8	0.004457167	72
11	2.2	0.00448468	78
12	2	0.004493851	80
13	1.6	0.004512194	84
14	1.3	0.00452595	87

Table (B-1) continue

15	1.2	0.004530536	88
16	1.2	0.004530536	88
17	1.2	0.004530536	88
18	1.2	0.004530536	88
19	1.2	0.004530536	88
20	1.2	0.004530536	88

Table (B-2) Effect of mechanical degradation on drag reduction effectiveness of PEO solution at 40 ppm concentration and 6m^3/h flow rate

Time (h)	**%DR**	***f***	**%Decrease**
0	19.5	0.003691378	0
1	18.1	0.003755576	7.2
2	17.4	0.003787675	10.8
3	16	0.003851873	17.9
4	15.8	0.003861044	18.9
5	15	0.003897728	23.1
6	14.3	0.003929827	26.7
7	12.8	0.003998611	34.4

Table (B-2) continue

8	12.7	0.004003196	34.9
9	11.7	0.004049052	40.00
10	11	0.004081151	43.6
11	10.1	0.004122421	48.2
12	9.3	0.004159105	52.3
13	8.7	0.004186619	55.4
14	7.5	0.004241646	61.5
15	7.3	0.004250817	62.6
16	7.5	0.004241646	61.5
17	7	0.004264573	64.1
18	6.4	0.004292087	67.2
19	5.9	0.004315015	69.7
20	5.2	0.004347113	73.3
21	4.4	0.004383798	77.4
22	4.9	0.00436087	74.9
23	4.1	0.004397555	78.9
24	4	0.00440214	79.5
25	3.5	0.004425068	82.1
26	3	0.004447996	84.6
27	4.3	0.004388384	77.9
28	3.9	0.004406726	80.0
29	3.7	0.004415897	81.0

Table (B-2) continue

30	3	0.004447996	84.6
31	2.8	0.004457167	85.6
32	2.5	0.004470924	87.2
33	2.3	0.004480095	88.2
34	3	0.004447996	84.6
35	2.8	0.004457167	85.6
36	2.5	0.004470924	87.2
37	2.4	0.004475509	87.7
38	2.8	0.004457167	85.6
39	1.9	0.004498437	90.3
40	2.6	0.004466338	86.7
41	2.2	0.00448468	88.7
42	1.8	0.004503023	90.8
43	1.6	0.004512194	91.8
44	1.5	0.004516779	92.3
45	1.6	0.004512194	91.8
46	1.4	0.004521365	92.8
47	1.7	0.004507608	91.3
48	1.3	0.00452595	93.3
49	1.5	0.004516779	92.3
50	1.2	0.004530536	93.8
51	1.6	0.004512194	91.8
52	1.3	0.00452595	93.3

Table (B-2) continue

53	1.5	0.004516779	92.3
54	1.3	0.00452595	93.3
55	1.2	0.004530536	93.8
56	1.2	0.004530536	93.8
57	1.2	0.004530536	93.8
58	1.2	0.004530536	93.8
59	1.2	0.004530536	93.8
60	1.2	0.004530536	93.8
61	1.2	0.004530536	93.8
62	1.2	0.004530536	93.8
63	1.2	0.004530536	93.8
64	1.2	0.004530536	93.8
65	1.2	0.004530536	93.8

Table (B-3) Effect of mechanical degradation on drag reduction effectiveness of Clay solution at 50 and 100 ppm concentrations and 6m^3/h flow rate

Time (h)	**%DR for 50 ppm**	**%DR for 100 ppm**
0	5.0	5.5
1	5.0	5.5
2	5.0	5.5
3	5.0	5.5
4	5.0	5.5
5	5.0	5.5
6	5.0	5.5
7	5.0	5.5
8	5.0	5.5
9	5.0	5.5
10	5.0	5.5
11	5.0	5.5
12	5.0	5.5
13	5.0	5.5
14	5.0	5.5
15	5.0	5.5

Table (B-4) Effect of mechanical degradation on drag reduction effectiveness of Alum solution at 50 and 100 ppm concentrations and 6m^3/h flow rate

Time (h)	**%DR for 50 ppm**	**%DR for 100 ppm**
0	11.0	14.5
1	11.0	14.5
2	10.8	14.5
3	11.0	14.5
4	11.0	14.5
5	11.0	14.5
6	11.0	14.5
7	10.8	14.5
8	11.0	14.5
9	11.0	14.5
10	11.0	14.5
11	11.0	14.5
12	11.0	14.5
13	11.0	14.5
14	11.0	14.5
15	11.0	14.5

Table (B-5) Effect of mechanical degradation on drag reduction effectiveness of SLES solution at 100 ppm concentration and 6m^3/h flow rate

Time (h)	%DR	*f*	%Decrease
0	11.7	0.004049	0
1	11.7	0.004049	0
2	11.7	0.004049	0
3	10	0.004127	14.5
4	8.3	0.004205	29.1
5	6	0.00431	48.7
6	5	0.004356	57.3
7	3.7	0.004416	68.4

Table (B-6) Effect of mechanical degradation on drag reduction effectiveness of SLES solution at 200 ppm concentration and 6m^3/h flow rate

Time (h)	%DR	*f*	%Decrease
0	13.5	0.003967	0
1	13.5	0.003967	0
2	13.5	0.003967	0
3	13.5	0.003967	0
4	12.8	0.003999	5.2
5	11	0.004081	18.5
6	10	0.004127	25.9
7	9.3	0.004159	31.1

Table (B-7) Effect of mechanical degradation on drag reduction effectiveness of SLES solution at 50 and 150 ppm concentration at 6m^3/h flow rate

Time (h)	**%DR for 50 ppm**	**%DR for 150 ppm**
0	10.5	12.8
1	9.8	12.8
2	8.6	12.8
3	7.5	11
4	5.7	9.8
5	4.4	8.2
6	2.5	7.2
7	1.7	5.8

Table (B-8) Effect of mechanical degradation on drag reduction effectiveness of Amylopectin solution at 50 ppm concentration and 6m^3/h flow rate

Time (h)	**%DR**	***f***	**%Decrease**
0	8.7	0.004187	0
1	7.9	0.004223	9.2
2	7.3	0.004251	16.1
3	6.6	0.004283	24.1
4	6.5	0.004288	25.3
5	5.8	0.00432	33.3
6	5.5	0.004333	36.8

7	4.9	0.004361	43.7
8	4.6	0.004375	47.1
9	4.3	0.004388	50.6
10	3.8	0.004411	56.3
11	3.8	0.004411	56.3
12	3.3	0.004434	62.1
13	3	0.004448	65.5
14	3.2	0.004439	63.2
15	2.7	0.004462	68.9

Table (B-9) Effect of mechanical degradation on drag reduction effectiveness of Amylopectin solution at 100 ppm concentration and 6m^3/h flow rate

Time (h)	**%DR**	***f***	**%Decrease**
0	9.8	0.004136	0
1	9.2	0.004164	6.1
2	8.7	0.004187	11.2
3	8.2	0.00421	16.3
4	7.4	0.004246	24.5
5	7.3	0.004251	25.5
6	6.8	0.004274	30.6

7	6.4	0.004292	34.7
8	5.8	0.00432	40.8
9	5.7	0.004324	41.8
10	5.4	0.004338	44.9
11	5.2	0.004347	46.9
12	4.8	0.004365	51.0
13	4.4	0.004384	55.1
14	4	0.004402	59.2
15	3.7	0.004416	62.2

Table (B-10) Effect of mechanical degradation on drag reduction effectiveness Admixture of (40 ppm PEO + 50 ppm Clay) additives at 6m^3/h flow rate

Time (h)	**%DR**	***f***	**%Decrease**
0	19.7	0.003682207	0
1	18.5	0.003737234	6.1
2	17.2	0.003796846	12.7
3	16.1	0.003847287	18.3
4	15.1	0.003893143	23.4
5	15.3	0.003883972	22.3

6	14.5	0.003920656	26.4
7	13.8	0.003952755	29.9
8	13.3	0.003975683	32.5
9	13	0.00398944	34.0
10	12.2	0.004026124	38.1
11	11	0.004081151	44.2
12	10.7	0.004094907	45.7
13	10	0.004127006	49.2
14	9.3	0.004159105	52.8
15	8.6	0.004191204	56.3

Table (B-11) Effect of mechanical degradation on drag reduction effectiveness solutions containing (40 ppm PEO + 100 ppm Clay) Co-additives at $6m^3/h$ flow rate

Time (h)	**%DR**	***f***	**%Decrease**
0	20	0.00366845	0
1	18.8	0.003723477	6
2	17.8	0.003769333	11
3	18	0.003760161	10
4	17.5	0.003783089	12.5
5	16.4	0.00383353	18

6	15.7	0.003865629	21.5
7	14.9	0.003902314	25.5
8	14.5	0.003920656	27.5
9	13.6	0.003961926	32
10	12.6	0.004007782	37
11	12.2	0.004026124	39
12	11.8	0.004044466	41
13	11.2	0.00407198	44
14	10.6	0.004099493	47
15	10	0.004127006	50

Table (B-12) Effect of mechanical degradation on drag reduction effectiveness solutions containing (40 ppm PEO + 10 ppm Alum) Co-additives at $6m^3/h$ flow rate

Time (h)	%DR	*f*	%Decrease
0	19.7	0.003682	0
1	18.2	0.003751	7.6
2	17.6	0.003779	10.7
3	16.7	0.00382	15.2
4	15.3	0.003884	22.3
5	14.7	0.003911	25.4

6	14.3	0.00393	27.4
7	13.9	0.003948	29.4
8	13.2	0.00398	32.9
9	12	0.004035	39.1
10	11.4	0.004063	42.1
11	10.8	0.00409	45.2
12	10.5	0.004104	46.7
13	10	0.004127	49.2
14	9.5	0.00415	51.8
15	8.5	0.004196	56.9

Table (B-13) Effect of mechanical degradation on drag reduction effectiveness solutions containing (40 ppm PEO + 50 ppm Alum) Co-additives at $6m^3/h$ flow rate

Time (h)	**%DR**	***f***	**%Decrease**
0	21.2	0.003613423	0
1	20.6	0.003640937	2.8
2	19.3	0.003700549	8.9
3	18.9	0.003718891	10.9
4	18.4	0.003741819	13.2
5	17.6	0.003778504	16.9

6	16.2	0.003842702	23.6
7	16	0.003851873	24.5
8	15.2	0.003888557	28.3
9	14.2	0.003934413	33.0
10	13.8	0.003952755	34.9
11	13	0.00398944	38.7
12	11.8	0.004044466	44.3
13	10.6	0.004099493	50.0
14	10.6	0.004099493	50.0
15	9.7	0.004140763	54.2

Table (B-14) Effect of mechanical degradation on drag reduction effectiveness solutions containing (40 ppm PEO + 100 ppm Alum) Co-additives at $6m^3/h$ flow rate

Time (h)	**%DR**	***f***	**%Decrease**
0	23.2	0.003521712	0
1	21.8	0.00358591	6.0
2	21.2	0.003613423	8.6
3	20	0.00366845	13.8
4	19.3	0.003700549	16.8
5	19.3	0.003700549	16.8
6	18.1	0.003755576	21.9

7	17.4	0.003787675	25.0
8	17.3	0.00379226	25.4
9	16.5	0.003828945	28.9
10	15.7	0.003865629	32.3
11	15.1	0.003893143	34.9
12	15	0.003897728	35.3
13	14.4	0.003925242	37.9
14	13.6	0.003961926	41.4
15	13	0.00398944	43.9

Table (B-15) Effect of mechanical degradation on drag reduction effectiveness solutions containing (40 ppm PEO + 100 ppm SLES) Co-additives at $6m^3/h$ flow rate

Time (h)	**%DR**	***f***	**%Decrease**
0	19.5	0.003691	-
1	21.8	0.003586	-
2	23.3	0.003517	0
3	22	0.003577	5.5
4	19.8	0.003678	14.9
5	17.6	0.003779	24.4
6	17	0.003806	26.9
7	16.1	0.003847	30.8

Table (B-16) Effect of mechanical degradation on drag reduction effectiveness solutions containing (40 ppm PEO + 200 ppm SLES) Co-additives at $6m^3/h$ flow rate

Time (h)	**%DR**	***f***	**%Decrease**
0	19.5	0.003691	-
1	22.4	0.003558	-
2	24.9	0.003444	-
3	25.1	0.003435	0
4	23.8	0.003494	5.2
5	22.8	0.00354	9.2
6	22	0.003577	12.4
7	21.1	0.003618	15.9

Table (B-17) Effect of mechanical degradation on drag reduction effectiveness solutions containing (40 ppm PEO + 50 ppm Amylopectin) Co-additives at $6m^3/h$ flow rate

Time (h)	**%DR**	***f***	**%Decrease**
0	20.6	0.003640937	0
1	19.8	0.003677621	3.9
2	18.5	0.003737234	10.2
3	17.8	0.003769333	13.6

4	17.2	0.003796846	16.5
5	17.2	0.003796846	16.5
6	16.4	0.00383353	20.4
7	15.9	0.003856458	22.8
8	15.3	0.003883972	25.7
9	14.7	0.003911485	28.6
10	14.3	0.003929827	30.6
11	13.8	0.003952755	33.0
12	13.4	0.003971097	34.9
13	13.2	0.003980268	35.9
14	12.7	0.004003196	38.4
15	12.1	0.00403071	41.3

Table (B-18) Effect of mechanical degradation on drag reduction effectiveness solutions containing (40ppm PEO + 100 ppm Amylopectin) Co-additives at 6m^3/h flow rate

Time (h)	**%DR**	***f***	**%Decrease**
0	21.8	0.00358591	0
1	21.1	0.003618009	3.2
2	19.6	0.003686792	10.1
3	18.8	0.003723477	13.8

4	19	0.003714306	12.8
5	18.5	0.003737234	15.1
6	18.1	0.003755576	16.9
7	17.7	0.003773918	18.8
8	17.2	0.003796846	21.1
9	16.9	0.003810603	22.5
10	16.5	0.003828945	24.3
11	15.6	0.003870215	28.4
12	15.5	0.0038748	28.9
13	15.2	0.003888557	30.3
14	14.8	0.003906899	32.1
15	14.5	0.003920656	33.5

Appendix C

Degradation Correlation of prediction equation 2.6 and Present work equation 4.1 with experimental data

Table (C-1) Degradation correlation of Polyethylene oxide and Clay for three solutions (40 ppm PEO, 40 ppm PEO+50 ppm clay, and 40 ppm PEO + 100 ppm clay)

Total concentration of additives (ppm)	Time (h)	DR(t)/DR(0) experimental	DR(t)/DR(0) predicted from eq.2.6	%error	DR(t)/DR(0) predicted from eq.4.1	%error
40	0	1	1	0	1.050376177	5.037618
40	1	0.9282051	0.376025438	59.48897	0.957608759	3.167795
40	2	0.8923077	0.36890313	58.65741	0.873034418	2.159936
40	3	0.8205128	0.364736497	55.54774	0.795929551	2.996086
40	4	0.8102564	0.361780435	55.34988	0.725634456	10.44385
40	5	0.7692308	0.359487802	53.26659	0.66154772	13.9988
40	6	0.7333333	0.357614845	51.23434	0.603120983	17.75623
40	7	0.6564103	0.356031477	45.76083	0.549854398	16.23312
40	8	0.6512821	0.354660064	45.54432	0.501292229	23.02993
40	9	0.6	0.353450567	41.09157	0.457018971	23.83017
40	10	0.5641026	0.352368742	37.53463	0.416655838	26.13828
40	11	0.5179487	0.351390272	32.15732	0.37985754	26.66117
40	12	0.4769231	0.350497067	26.50868	0.346309185	27.38678
40	13	0.4461538	0.349675506	21.62446	0.315723777	29.23433
40	14	0.3846154	0.348914951	9.282113	0.287839592	25.16171
40	15	0.374359	0.348206937	6.985818	0.262418121	29.90201
90	0	1	1	0	1.050376177	5.037618
90	1	0.9390863	0.376025438	59.95837	0.964781523	2.736195
90	2	0.8730964	0.36890313	57.74772	0.886161923	1.496453

90	3	0.8172589	0.364736497	55.37075	0.813949049	0.404992
90	4	0.7664975	0.361780435	52.80083	0.747620761	2.462722
90	5	0.7766497	0.359487802	53.71301	0.686697543	11.58208
90	6	0.7360406	0.357614845	51.41371	0.630738854	14.30651
90	7	0.7005076	0.356031477	49.17522	0.579340279	17.29708
90	8	0.6751269	0.354660064	47.46764	0.532130122	21.18073
90	9	0.6598985	0.353450567	46.43864	0.488767117	25.93298
90	10	0.6192893	0.352368742	43.10111	0.448937744	27.50759
90	11	0.5583756	0.351390272	37.0692	0.412354022	26.15114
90	12	0.5431472	0.350497067	35.46923	0.378751516	30.26724
90	13	0.5076142	0.349675506	31.11393	0.347887248	31.46621
90	14	0.4720812	0.348914951	26.09006	0.319538087	32.3129
90	15	0.4365482	0.348206937	20.23632	0.293499082	32.76823
140	0	1	1	0	1.050376177	5.037618
140	1	0.94	0.376025438	59.99729	0.971961617	3.400172
140	2	0.89	0.36890313	58.55021	0.899401069	1.0563
140	3	0.9	0.364736497	59.47372	0.83225745	7.52695
140	4	0.875	0.361780435	58.65366	0.770126343	11.98556
140	5	0.82	0.359487802	56.16002	0.71263355	13.09347
140	6	0.785	0.357614845	54.44397	0.659432769	15.99583
140	7	0.745	0.356031477	52.21054	0.610203683	18.09347
140	8	0.725	0.354660064	51.08137	0.564649701	22.11728
140	9	0.68	0.353450567	48.02198	0.522496521	23.16228
140	10	0.63	0.352368742	44.06845	0.483490199	23.25552
140	11	0.61	0.351390272	42.39504	0.447395861	26.65642
140	12	0.59	0.350497067	40.59372	0.4139961	29.83117
140	13	0.56	0.349675506	37.55795	0.383089751	31.59112
140	14	0.53	0.348914951	34.16699	0.354490668	33.11497
140	15	0.5	0.348206937	30.35861	0.328026623	34.39468
			AAPE	41.56112	AAPE	18.04919

Table (C-2) Degradation correlation of Polyethylene oxide and Alum for three solutions (40 ppm PEO, 40 ppm PEO+50 ppm Alum, and 40 ppm PEO + 100 ppm Alum)

Total concentration of additives (ppm)	Time (h)	DR(t)/DR(0) experimental	DR(t)/DR(0) predicted from eq.2.6	%error	DR(t)/DR(0) predicted from eq.4.1	%error
40	0	1	1	0	1.298673987	29.8674
40	1	0.9282051	0.374844	59.61623	1.184185147	27.57796
40	2	0.8923077	0.368863	58.66195	1.079789519	21.01089
40	3	0.8205128	0.365363	55.47135	0.984597206	19.99778
40	4	0.8102564	0.362881	55.2141	0.897796869	10.80404
40	5	0.7692308	0.360955	53.07584	0.818648696	6.42433
40	6	0.7333333	0.359382	50.99337	0.746478081	1.792466
40	7	0.6564103	0.358052	45.45302	0.680669904	3.695806
40	8	0.6512821	0.3569	45.20039	0.620663285	4.701307
40	9	0.6	0.355884	40.68599	0.565946698	5.67555
40	10	0.5641026	0.354975	37.07256	0.516053855	8.517726
40	11	0.5179487	0.354153	31.62387	0.470559478	9.149408
40	12	0.4769231	0.353403	25.8994	0.429075778	10.0325
40	13	0.4461538	0.352713	20.94371	0.391249239	12.3062
40	14	0.3846154	0.352074	8.460846	0.356757402	7.243075
40	15	0.374359	0.351479	6.111823	0.325306296	13.10311
90	0	1	1	0	1.298673987	29.8674
90	1	0.9716981	0.374844	61.4238	1.19122541	22.59213
90	2	0.9103774	0.368863	59.48245	1.092666864	20.02351
90	3	0.8915094	0.365363	59.01745	1.002262712	12.42312
90	4	0.8679245	0.362881	58.18984	0.919338405	5.923773
90	5	0.8301887	0.360955	56.52132	0.843275011	1.576308

90	6	0.7641509	0.359382	52.96977	0.773504853	1.224092
90	7	0.754717	0.358052	52.55811	0.709507287	5.990285
90	8	0.7169811	0.3569	50.22184	0.650804698	9.229871
90	9	0.6698113	0.355884	46.86802	0.596958935	10.87655
90	10	0.6509434	0.354975	45.46757	0.547568321	15.88081
90	11	0.6132075	0.354153	42.24577	0.502264082	18.09232
90	12	0.5566038	0.353403	36.50728	0.460708171	17.2287
90	13	0.5	0.352713	29.45747	0.422590494	15.4819
90	14	0.5	0.352074	29.58527	0.387626588	22.47468
90	15	0.4575472	0.351479	23.18195	0.355555475	22.29097
140	0	1	1	0	1.298673987	29.8674
140	1	0.9396552	0.374844	60.10832	1.198262095	27.52147
140	2	0.9137931	0.368863	59.63391	1.105613947	20.99171
140	3	0.862069	0.365363	57.61786	1.020129323	18.335
140	4	0.8318966	0.362881	56.37911	0.941254139	13.14558
140	5	0.8318966	0.360955	56.61058	0.868477583	4.397305
140	6	0.7801724	0.359382	53.93557	0.801327944	2.711648
140	7	0.75	0.358052	52.25974	0.739370286	1.417295
140	8	0.7456897	0.3569	52.13826	0.682203114	8.513802
140	9	0.7112069	0.355884	49.96055	0.629455984	11.49467
140	10	0.6767241	0.354975	47.54505	0.580787241	14.17666
140	11	0.6508621	0.354153	45.58705	0.535881519	17.66589
140	12	0.6465517	0.353403	45.34035	0.494447798	23.52541
140	13	0.6206897	0.352713	43.17407	0.456217706	26.49826
140	14	0.5862069	0.352074	39.94037	0.420943528	28.19199
140	15	0.5603448	0.351479	37.27455	0.38839671	30.68613
			AAPE	42.82683	AAPE	14.6295

Table (C-3) Degradation correlation of Polyethylene oxide and Amylopectin for three solutions (40 ppm PEO, 40 ppm PEO+50 ppm Amylopectin, and 40 ppm PEO + 100 ppm Amylopectin)

Total concentration of additives (ppm)	**Time (h)**	**DR(t)/DR(0) experimental**	**DR(t)/DR(0) predicted from eq.2.6**	**%error**	**DR(t)/DR(0) predicted from eq.4.1**	**%error**
40	**0**	**1**	**1**	**0**	**0.981361151**	**1.863885**
40	**1**	**0.928205**	**0.3807614**	**58.97874**	**0.920862019**	**0.791108**
40	**2**	**0.892308**	**0.3699894**	**58.53567**	**0.864092588**	**3.162038**
40	**3**	**0.820513**	**0.3636868**	**55.67567**	**0.810822845**	**1.180966**
40	**4**	**0.810256**	**0.3592157**	**55.66642**	**0.760837138**	**6.099214**
40	**5**	**0.769231**	**0.3557484**	**53.7527**	**0.713932872**	**7.188727**
40	**6**	**0.733333**	**0.3529163**	**51.87505**	**0.669920266**	**8.647236**
40	**7**	**0.65641**	**0.3505225**	**46.60009**	**0.628620863**	**4.23354**
40	**8**	**0.651282**	**0.3484494**	**46.49792**	**0.589867532**	**9.429788**
40	**9**	**0.6**	**0.3466214**	**42.22976**	**0.553503335**	**7.749444**
40	**10**	**0.564103**	**0.3449866**	**38.84328**	**0.519380867**	**7.927937**
40	**11**	**0.517949**	**0.3435082**	**33.6791**	**0.487361968**	**5.905363**
40	**12**	**0.476923**	**0.3421589**	**28.257**	**0.457316995**	**4.110953**
40	**13**	**0.446154**	**0.3409179**	**23.58736**	**0.429124236**	**3.816982**
40	**14**	**0.384615**	**0.3397693**	**11.65998**	**0.402669519**	**4.694075**
40	**15**	**0.374359**	**0.3387002**	**9.525296**	**0.377845675**	**0.931379**
90	**0**	**1**	**1**	**0**	**0.981361151**	**1.863885**
90	**1**	**0.961165**	**0.3807614**	**60.38543**	**0.942696035**	**1.921524**
90	**2**	**0.898058**	**0.3699894**	**58.80118**	**0.905554235**	**0.834688**
90	**3**	**0.864078**	**0.3636868**	**57.9104**	**0.869875848**	**0.671025**
90	**4**	**0.834951**	**0.3592157**	**56.97766**	**0.835603178**	**0.078055**
90	**5**	**0.834951**	**0.3557484**	**57.39292**	**0.80268085**	**3.864968**

90	**6**	**0.796117**	**0.3529163**	**55.67027**	**0.771055579**	**3.147897**
90	**7**	**0.771845**	**0.3505225**	**54.5864**	**0.740676403**	**4.038152**
90	**8**	**0.742718**	**0.3484494**	**53.08459**	**0.711494088**	**4.204064**
90	**9**	**0.713592**	**0.3466214**	**51.42584**	**0.683461607**	**4.222387**
90	**10**	**0.694175**	**0.3449866**	**50.30262**	**0.656533539**	**5.422441**
90	**11**	**0.669903**	**0.3435082**	**48.72268**	**0.630666435**	**5.857039**
90	**12**	**0.650485**	**0.3421589**	**47.39945**	**0.60581851**	**6.866707**
90	**13**	**0.640777**	**0.3409179**	**46.79614**	**0.581949532**	**9.180603**
90	**14**	**0.616505**	**0.3397693**	**44.88781**	**0.559020996**	**9.324153**
90	**15**	**0.587379**	**0.3387002**	**42.33699**	**0.536995888**	**8.57756**
140	**0**	**1**	**1**	**0**	**0.981361151**	**1.863885**
140	**1**	**0.96789**	**0.3807614**	**60.66067**	**0.964903176**	**0.308582**
140	**2**	**0.899083**	**0.3699894**	**58.84811**	**0.94872123**	**5.521035**
140	**3**	**0.862385**	**0.3636868**	**57.82781**	**0.932810664**	**8.166343**
140	**4**	**0.87156**	**0.3592157**	**58.78473**	**0.917166948**	**5.232839**
140	**5**	**0.848624**	**0.3557484**	**58.07937**	**0.901785553**	**6.26446**
140	**6**	**0.830275**	**0.3529163**	**57.49406**	**0.886662126**	**6.79135**
140	**7**	**0.811927**	**0.3505225**	**56.82831**	**0.871792316**	**7.373291**
140	**8**	**0.788991**	**0.3484494**	**55.83606**	**0.857171834**	**8.641546**
140	**9**	**0.775229**	**0.3466214**	**55.28789**	**0.842796624**	**8.715777**
140	**10**	**0.756881**	**0.3449866**	**54.41995**	**0.828662455**	**9.483888**
140	**11**	**0.715596**	**0.3435082**	**51.99692**	**0.814765334**	**13.85823**
140	**12**	**0.711009**	**0.3421589**	**51.877**	**0.801101267**	**12.67102**
140	**13**	**0.697248**	**0.3409179**	**51.10519**	**0.78766638**	**12.96794**
140	**14**	**0.678899**	**0.3397693**	**49.9529**	**0.774456799**	**14.07539**
140	**15**	**0.665138**	**0.3387002**	**49.07818**	**0.761468709**	**14.48288**
			AAPE	**46.46087**	**AAPE**	**5.92138**

اوضحت التجارب العمليه لدراسه المعدل الزمني للانحلال ان المنظف الايوني SLES يحافظ على فعاليته خلال وقت معين يعتمد على تركيز المنظف الايوني ثم يبدأ بفقدان فعاليته تدريجيا وذلك بسبب تغير شكل ارتباط الجزيئات مع بعضها في الجريان المضطرب. بالاضافه الى ذلك فان المنظف الايوني قادر على استعاده فعاليته خلال فترة توقف الجريان.

بينت التجارب وبصورة عامه زيادة تدريجيه في نسبه تخفيض الاعاقه عند خلط الطين، الشب، والاميلوبكتين مع البولي اثيلين اوكسايد كمضافات مشتركه. اما المنظف الايوني مع البولي اثيلين اوكسايد فانه يزيد معدل تقليل الاعاقه نتيجه تكون تجمع جزيئات المنظف الايوني مع البولي اثيلين اوكسايد. كل المضافات المشتركه تعمل على تقليل قابليه الانحلال مع الزمن عند الجريان المضطرب. وان زيادة تركيز المضافات المشتركه يعمل على تقليل قابليه الانحلال.

تم تحليل سلوك الانحلال الميكانيكي لثلاث انواع من المحاليل التي تحتوي على البولي اثيلين اوكسايد مع الطين، البولي اثيلين اوكسايد مع الشب، والبولي اثيلين اوكسايد مع الاميلوبكتين كداله للزمن، ونسبه البولي اثيلين اوكسايد بالمحلول من خلال تطوبر معادله fractional exponential decay واتضح ان المعادلة المطورة تطابق النتائج العمليه بدرجه افضل.

الخلاصه

تهدف التجارب العمليه الى دراسه خصائص انواع مختلفه من المضافات التي تعمل على تقليل الاعاقه للجريان المضطرب في كل من الاضافه المنفردة والمشتركه. في هذا البحث تم استخدام نوعين من البوليمرات ذات الاوزان الجزيئيه العاليه وقابله للذوبان في الماء. وهي اوكسيد البولي اثيلين ذي السلاسل الطويله المرنه بوزن جزيئي $١٠^{٦}$ × ٧ غرام/ مول و الاميلوبكتين باعتباره نوع من البوليمرات الصلبه السليلوزيه. بالاضافه الى استخدام نوع معين من الطين الطبيعي هو الكاولين ومادة سلفات الالمنيوم (الشب) كجزيئات عالقه اومتجمعه بالمحلول والمنظف الايوني صوديوم لوريال ايثر سلفيت. تم دراسه خصائص المضافات باستخدام منظومه تدوير مغلقه بالجريان المضطرب للماء.

لقد اوضحت التجارب ان البوليمر اوكسيد البولي اثيلين يتمتع بفعاليه عاليه في تقليل الاعاقه للجريان المضطرب وذلك بسبب وزنه الجزيئي العالي مما يساعده على التشابك والتداخل عند الجريان المضطرب. حيث يتعرض اوكسيد البولي اثيلين للتحلل الميكانيكي عند الجريان المضطرب ويزداد معدل الانحلال بنقصان تركيز البوليمر.

يعد الشب معامل جيد في تقليل الاعاقه بسبب تداخل جزيئاته مع الماء بشكل يسمح باخماد الجريان المضطرب. اما الطين فانه يعمل على تقليل الاعاقه بمعدل اقل من الشب. وان كل من المادتين لاتتأثر بالمؤثرات الميكانيكيه ولا تفقد فعاليتها مع الزمن خلال ١٥ ساعه من التدوير في المنظومه تحت تأثير الجريان المضطرب وذلك نتيجه استقرارالشكل المتكون من المادة الغرويه او الجزيئات العالقه بالماء.

يتمتع كل من المنظف الايوني والبوليمر الاميلوبكتين بفعاليه متوسطه في تقليل الاعاقه. تعود فعاليه المنضف الايوني الى تداخل جزيئاته مع الماء. اما الاميلوبكتين فيعود سبب فعاليته الى خصائصه المطاطيه وتكوينه طبقه خفيفه على الجدار. اضافه الى ذلك فان الاميلويكتين يفقد فعاليته مع الزمن بسبب تكسر سلاسل البوليمر كما في اوكسيد البولي اثيلين.

شكر وتقدير

الحمد لله رب العالمين الذي ساعدني وأعانني على أكمال هذا البحث الذي أرجو أن أنال به حسن القبول.

لو أنني أوتيت كل بلاغه وأفنيت بحر النطق في النظم والنثر لما كنت بعد القول إلا مقصرة ومعترفة بالعجزعن واجب الشكر الى أستاذي الفاضل المشرف الدكتور **جابر شنشول الجمالي** لما بذله من جهد في توجيهي ومتابعتي ولقد أثرى هذا البحث برأيه السديد وعلمه الوفير مما كان له الاثر الكبير في انجاز هذا البحث فبارك الله جهوده وسدد بالخير والعطاء دربه.

يشرفني ان اتقدم بالشكر الجزيل الى استاذي الدكتور **باسم عبيد حسن** المحترم رئيس قسم الهندسه الكيمياويه وشكري وأمتناني الى كافه منتسبي القسم وزملائي الذين لم يقصروا في مساعدتي والى كل من مد لي يد العون وساعدني.

كما اود أن أتقدم بالشكر والتقدير الى السيد عميد كلية الهندسة في جامعة النهرين لما أبداه من الدعم و المساعدة.

كما واتقدم بالشكر والاجلال الى والدي الكريمين اللذان حفوني بالدموع والدعاء وأخوتي الذين كانوا خير سند لي في تذليل العقبات.

لبنى عبد الكريم نعيم

تأثير الاضافات المشتركة على مقاومة الانحلال لمحاليل البوليمر المخففة تحت تأثير الجريان المضطرب

رسالة
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وهي جزء من متطلبات نيل درجة ماجستير علوم
في الهندسه الكيمياويه

من قبل
لبنى عبد الكريم نعيم الغزي
بكالوريوس علوم في الهندسه الكيمياويه ٢٠٠٨

جمادي الاول ١٤٣٢
نيسان ٢٠١١