PREPARATION AND CHARACTERIZATION OF POLY (ACRYLATE) EMULSION FOR POUR POINT DEPRESSANT APPLICATION

by

AHMAD SHAIFUL B. ABD RAZAK

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Bismillahirrahmanirrahim

"In the name of God, the Most Gracious, the Most Merciful.

All praises are due to Allah the Lords of the worlds, the Entirely Merciful and the Especially Merciful. The grateful gratitude only belongs to Him for bestowing me the great opportunities and experiences in this life and for His blessings. Not to mention the praise to His Messenger, Prophet Muhammad (blessings and peace of Allah be upon him) and his family for the greatest love and Islam.

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TABLE OF CONTENT

CHAPTER ONE: INTRODUCTION

CHAPTER TWO: LITERATURE REVIEW

CHAPTER THREE: METHODOLOGY

CHAPTER FOUR: RESULTS AND DISCUSSIONS

4.1 Characterization of emulsion poly (acrylate) pour point depressant

4.2 Physicochemical, thermal and performance characterization of emulsion poly (acrylate) as pour point depressant

4.3 Evaluation of emulsion poly (acrylate) pour point depressant destabilization

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

LIST OF PUBLICATIONS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

%	Percentage
ml	Mililiter
mL/min	Mililiter per minutes
cP	Centi Poise
µL	Micro liter
Δ	Delta
wt. %	Weight percent
mm	Millimetre
µm	Micrometre
nm	Nano metre
cm^{-1}	Per centimetre
g	Gram
gmol^{-1}	Gram per mole
h	Hour
min	Minute
s	Second
^{o}	Degree
^{o}/min	Degree per minute
^{o}C	Degree Celsius
^{o}C/min	Degree Celsius per minute
Tg	Glass transition temperature

LIST OF ABBREVIATIONS

PPD	Pour point depressant
WAT	Wax appearance temperature
EVA	Ethylene vinyl acetate
MA	Methacrylate
MMA	Methyl methacrylate
PMA	Poly methacrylate
PMMA	Poly methyl methacrylate
FTIR	Fourier transform infrared
GPC	Gel permeation chromatography
SEM	Scanning electron microscopy
ppm	Part per million
rpm	Rotation per minute
DSC	Differential scanning calorimeter
M_n	Average number molecular weight
M_w	Average weight molecular weight
PDI	Polydispersity index
PSD	Particles size distribution
MWD	Molecular weight distribution
F/T	Freeze thaw

PENGHASILAN DAN PENCIRIAN POLI (AKRILAT) EMULSI UNTUK APLIKASI PENEKANAN TITIK TUANG

ABSTRAK

Agen penekanan titik tuang (PPD) dalam bentuk emulsi mendapat perhatian yang meluas dalam menyelesaikan isu pemejalan pada suhu yang rendah yang dihadapi oleh PPD konvensional. Dengan menggunakan melalui sistem pempolimeran untuk menghasilkan emulsi PPD, kemampuan PPD untuk mengalir pada suhu rendah dapat dicapai. Objektif utama ujikaji ini dilakukan adalah untuk mengukuhkan korelasi antara parameter proses dan sifat partikel terhadap kestabilan dan prestasi emulsi poli(akrilat) PPD. Penyelidikan ini menumpukan terhadap kesan kepekatan monomer terhadap pelbagai kesan pengeluaran seperti berat molekul, saiz partikel, kimia fizikal, prestasi, dan korelasi antara kepekatan monomer dan keadaan simpanan terhadap kestabilan emulsi. Dua jenis akrilat monomer digunakan, metakrilat dan metil metakrilat. Penyediaan emulsi akrilat divariasikan berdasarkan kepekatan monomer dari 10 wt. % to 30 wt. %. Sampel PPD dicirikan menggunakan spektrum Fourier Transform Infrared (FTIR) dan alat gel penyerapan kromatografi (GPC). Prestasi PPD dinilai menerusi analisis titik tuang, sifat kimia-fizikal, kesan haba, potensi zeta, dan penilaian saiz zarah. Peningkatan kepekatan monomer menghasilkan nilai purata berat molekul yang tinggi sehingga nilai kepekatan monomer optima 20 wt. %. Nilai berat molekul yang paling tinggi ialah 4.09 x 10^7 g/mol untuk kepekatan monomer 20 wt. % emulsi metilmetakrilat. Saiz zarah untuk kedua-dua jenis emulsi poli(akrilat) PPD menunjukkan peningkatan dibawah pengaruh kepekatan monomer. Saiz zarah paling kecil ialah 64nm diperoleh dari emulsi metakrilat dengan kepekatan monomer 10 wt. %. Kestabilan PPD untuk

sampel 10 wt. %, 15 wt. % dan 20 wt. % menunjukkan kestabilan yang sangat baik dengan kemampuan untuk mengekalkan kestabilan koloid selepas 15 kitaran sejuk-cair. Pemerhatian dalam penyelidikan menunjukkan dengan memanipulasikan berat molekul menerusi kepekatan monomer kemudiannya menjejaskan agihan berat molekul, saiz dan agihan zarah PPD yang kemudiannya menyumbang kepada kestabilan dan prestasi sistem emulsi PPD. Lanjutan dari itu, ujikaji prestasi menunjukkan peningkatan yang mengesahkan kepekatan monomer adalah antara faktor utama yang menyumbang kepada peningkatan prestasi titk tuang emulsi PPD.

PREPARATION AND CHARACTERIZATION OF POLY (ACRYLATE) EMULSION FOR POUR POINT DEPRESSANT APPLICATION

ABSTRACT

Emulsion pour point depressant (PPD) is gaining extensive consideration in solving the solidification issue of conventional PPD at lower temperature. By producing PPD emulsion via polymerization system, low-temperature flow ability of PPD can be achieved. The main objective of this study is to establishing the correlation between process parameter and particles properties towards stability and performance of emulsion poly (acrylate) PPD. This study considered the effects of monomer loading towards various outputs, i.e. molecular weight, particle size, physicochemical, performance and the correlation between monomer loading and storage condition on the emulsion stability. Two type of acrylate monomer were used, methacrylate (MA) and methylmethacrylate (MMA) respectively. The monomer loading of the prepared acrylate emulsion were varied from 10 wt. % to 30 wt. %, respectively. PPD samples were characterized using Fourier Transform Infrared Spectroscopy (FTIR) and Gel Permeation Chromatography (GPC) unit. The performance of the PPD samples were evaluated by taking measurements of the pour point, physicochemical, thermal, zeta potential and particle size measurement. The increment of monomer loading resulted in a higher average molecular weight up to an optimum monomer loading of 20 wt.%. The value of the highest molecular weight, obtained was 4.09 x 107 g/mol for methyl methacrylate emulsion of 20 wt. % monomer loading. The particle size of the both emulsion poly (acrylate) PPD samples shows increment trends under the influence of monomer loading. The smallest particle size obtained was 64nm for sample methacrylate emulsion (10 wt.

%). The stability of PPD 10 wt. %, 15 wt. % and 20 wt. % was found to have excellent stability with the ability to maintain its colloidal stability after 15 cycles of freeze thaw. The findings showed by manipulating the molecular weight through monomer loading subsequently affected the molecular weight distribution, size and distribution of PPD particle which subsequently contributed to the stability and performance of the PPD emulsion system. Furthermore, the performance analysis showed increment trends confirming that monomer loading is among the principal factor that contributes to the increment of emulsion PPD pour point performance.

CHAPTER ONE

INTRODUCTION

1.1 Research background

Oil and gas industry has started following the discovery at Oil Creek Pennsylvania in 1859, continued with Texas in 1901. From the time when crude oil was discovered, it puts them in the frontline of the energy resources. During 20th century, technological breakthrough has influence the application of crude oil. Automobile and electrical light bulbs are the main subject that contributed to the revolution.

Starting from Rockefeller’s era till existence of seven major company, countless technologies have been used to improvised the production either upstream or downstream industry. Over hundred years since crude oil discovery, numerous issues rise related to the transportation, demand, discovery area, production and etc. Basic concern about demand correlates with the capability of exporters to achieve those demands. In order to meets the world demand, exporters has to increase their annual production volume which eventually contribute to several challenges *i.e.* throughout extraction and pipeline transport of waxy crude oils.

Inspire from that challenges, proper scheduling of crude oil transportation will affect enormous potential such as economic, technical and others. As example, in pipeline transportation systems, flow ability and pipeline clogging is the most concern matter in crude oil transportation from offshore to the refinery. To be precise, transportation from processing wells to the enhanced oil recovery reservoir often obstructed due to high viscosity and low pour point of crude oil.

The oil field exploration has become more challenging due to the offshore operation with increasing water depth and cooler environment. This situation is mainly related to the surrounding condition such as extreme temperature changes which has noticeable effect on crude oil flow characteristic. **Figure 1.1** illustrated pipeline clogging and wax deposition effect during crude oil transportation. At low temperature condition, wax deposition tends to occur and subsequently increased the crude oil viscosity. The temperature which paraffin wax susceptible to crystallize or deposit known as pour point temperature. This wax deposition leads to reduction of effective diameter of the pipelines, eventually pipeline became clogged.

Figure 1.1: Pipeline clogging during crude oil transportation (Yang et al. 2015)

Lot of approaches has been implemented to overcome the reoccurring wax problems have been proposed and used *i.e.* heating the pipelines, pipeline pigging, wax removing chemical and others. However, almost all methods are only act as the corrective action for the problem where it is only applicable after the clogging has occurred. Besides, those methods are all time and energy consuming where the pipeline heating device need some extra cost and energy consumption. Preferably, wax prevention chemical is applied in the oil field as it more economical compared to others. Normally, the wax prevention chemicals are made up from polymeric based chemical and later will assimilated with crude oil in the pipeline (Norland and Kelland, 2012).

The usage of chemical wax prevention did not give significant effect to the oil, but only results in the pour point reduction. With respect to the pour point measurement on the results of the previous study, it can be concluded that latest pour point reduction recorded in range 5 to 25 ˚C. But most ppd used were derived from copolymer and tripolymer material. The chemicals used need to have similar structure with paraffin, so it can interact with the paraffin and prevent agglomeration (Atta et al., 2015). They further explain that the chemical should have polar functional group so it can repulse each other to co-crystallize with paraffin and dispersed them in crude oil.

In oil and gas related industry, there are three common types of chemical wax prevention which are wax dispersant, wax modifier (inhibitor) and pour point depressant (flow improver). Wax dispersant chemical is used to prevent wax deposition from stick on the pipeline by keeping the wax precipitate dispersed as separated particles (Norland and Kelland, 2012). The wax modifiers are chemicals that will affect the wax appearance temperature (WAT) of the crude oil.

Pour point depressant (PPD) are used for lowering the pour point temperature and improved the flow properties of the crude oil. A few types of PPD are commonly developed and used (*i.e.* ethylene copolymer and comb polymer) by various industries. Common type of ethylene copolymers is used as PPD is ethylene vinyl acetate (EVA). Comb polymer referred to polymeric materials with long pendant group structure. It consists of a polyvinyl backbone with different pendant chains, which are normally long alkyl chains (Norland and Kelland, 2012). Commonly used polymer as pour point depressant belongs to acrylate family.

Generally, commercialized polymer was used as main parts in conventional PPD production. In PPD production process, the polymer needs to be dissolved and heated before it is suitable to be injected in the oil field pipelines. The shortcomings of this process are time consuming and extra costs were required. Admiral et al. (2016) explained that traditional PPDs tend to solidify at room temperature and required the crude oil producer to heat up the PPD or diluted it with solvent. Suitable solvent are necessary to dissolve the polymer. Solvent which can cause increase the pipeline corrosion rates need to be avoided as well as solvent which can cause harmful effect to the environment.

1.2 Problem statement

Currently, emulsified PPD is the best solution available for this problem. This is due to the reduction of the solvent usage in the PPD as the emulsion mainly consists of water. Additionally, the emulsified PPD exhibit good flow ability properties at room condition and even flow able at lower temperature (<25 °C). These PPD emulsions are superior in cold climate application where flow properties are critical. Current emulsified PPD production consists of two stage process. Initially, polymer solution is prepared via dilution process. Then, the process continues with the polymer emulsification stage.

Even though, the conventional emulsification methods are well studied and robust, this method has limitation in producing consistent particle size and particle size distribution. Many interesting methods have been proposed to overcome the problem throughout this decade. As example, Zhang et al. (2010) prepared monodisperse latex particle using two stage swelling seeded polymerization method. Though these methods successfully produce required particle size in laboratory scale, these methods significantly challenging in producing massive industrial scale due to the limitation of productivity charge and efficiency. The simplest method to overcome this limitation is by using one step emulsion polymerization to prepare monodisperse polymeric nanoparticles.

In PPD application, molecular weight (Mw) and molecular weight distribution (Dp) have significant influence towards PPD performance in hindering the wax formation. However, current emulsified PPD are unable to control specific molecular weight of PPD. Besides Mw, particle size also plays a certain role in PPD's stability and its application. According to Totten et al. (2003), broad molecular weight polymer is among the ideal characteristic needed for PPD application. While, Wilburn and Heilman (1989) stated that molecular weight of 10,000 to 300,000 for polymer PPD has the capability to achieve good pour point depressancy. High molecular weight of polymeric nanoparticle dispersions i.e. Polyacrylamide ((Tamsilian et al., 2016), Polylactide-co-glycolide (Dinarvand et al., 2011), Polyacetylene (Müller et al., 2006) are example of products with various application prospects.

Now days, lot of attention is given related to producing wide range of molecular weight polymeric emulsion but not in nano size. Especially, in oil and gas industry and the materials are used in various applications i.e. drilling fluid and flow-ability agent in enhanced oil recovery. In theory, smaller particle size PPD provide higher surface area to volume ratio, thus results in more contact between the PPD and crude oil. Nanoparticles exhibit potential application in polymer modification due to unique size, high surface area and quantum tunnelling effects (Yang et al (2015).

Many studies have investigated on methodology and materials that improve the product performance such as low temperature properties (He et al., 2016; Ma et al., 2015). According to previous works, polymer derived from acrylate group *i.e.* poly methacrylate has proven to be an effective cold flow additive especially for biodiesel and diesel application (J. Wang et al., 2014).

Unfortunately, there is insufficient technical data in previous study discussing high molecular weight poly (acrylate) and the effects of acrylate-based pour point depressant on the cold flow properties. Therefore, acrylate homo-polymer was selected and study on the impact of preparation parameter towards stability need to be researched further.

In this work, PPD production approaches being improved through single stage direct polymer emulsion method. This method involved emulsion polymerization process and water acts as continuous phase. In general, this method is oil in water (O/W) emulsion system. The reason behind water selection as continuous phase is due to good interaction with various monomers, cheap, non-toxic and environmental friendly. Moreover, through this preparation method, the control towards molecular weight and particles size (*range below 200 nm*) can be done. The PPD emulsion molecular weight is being control through the monomer loading and the particle size of the PPD is being control by performing emulsion polymerization method.

1.3 Objectives and scope of the research

This research will starts with the preparation of emulsions from acrylate monomer. Several tasks were undertaken as a part of this research project starting from monomer selections, emulsions preparation, characterizations, applied analysis and destabilization effect.

The objectives of this study are as follows: -

- To study and observation the effect of different monomer loadings towards properties and morphology in emulsion poly (acrylate) pour point depressant.
- To establish the effect of monomer type towards emulsion stability and physico-chemical characteristics of emulsion poly (acrylate) pour point depressant particle.
- To assess impact of monomer loading on different isothermal aging and freeze thaw in emulsion poly (acrylate) pour point depressant destabilization.

1.4 Thesis outline

In this thesis, there are five chapters discussed on emulsion poly (acrylate) as pour point depressant (PPD).

In first chapter, flow ability provides significant problem in the crude oil and the pipeline clogging is the subject matter which resulting to the deposited wax produced under low temperature condition. Common corrective and preventive action taken to overcome the situation has been discussed. PPD has been highlighted as most efficient preventive chemical existed nowadays and widely used to prevent those problems. Then, the problems related to the conventional PPD and emulsified PPD which available on the market today being highlighted. Therefore, the improvement of current PPD properties can be reached. The improvement on the PPD production method which is the PPD emulsion provides better control in term of its molecular weight and particles size which give positive effect towards the PPD properties and performance.

For the second chapter, a literature review of all related elements and aspects which is related to the on-going research is stated. This literature review contains all relevant and specific information regarding past and recent development in PPD technology. Basically, the sources of gaining such information are from journals, books, online forums as well as previous thesis written by former students.

In the third chapter, the study methodology which includes all required apparatus and equipment in conducting this study. Experimental methodology is arranged and designed to accomplish the objectives. Type of testing and element that are needed to be emphasized during each testing such as FTIR, DSC, Particle Size, GPC and pour point test are stated.

Proceeding with chapter 4, experimental results are presented in charts, data tables, and micrographs. The results obtained from the experiments are evaluated and discussed thoroughly. It stated detail explanations based on previous study, experiment and other polymeric literature to describe how such result can be obtained. There are all three topics in chapter four which are; i) Characterization of Emulsion Poly(acrylate) Pour Point Depressant, ii) Physicochemical, Thermal and Performance of Emulsion Poly(acrylate) as Pour Point Depressant and iii) Emulsion Destabilization Evaluation of Emulsion Poly(acrylate).

Each topic represents the research objectives. In the first sub-topic, discussion on the characterization analysis has done on the Emulsion Poly (acrylate) samples for instance the structure conformation test through FTIR and molecular weight analysis through GPC. The second topic will be focusing on the properties of Emulsion Poly (acrylate) as PPD where the flow-ability and the PPD performance were tested and discussed. The third topic was a discussion on the stability of the emulsion at two different conditions which are at isothermal condition and under freeze thaw cycles.

The final chapter will include overall conclusion and stated whether the objectives of study are achieved. In this chapter as well, recommendation is stated in how to improve the experiment for the future study. The recommendation includes precaution steps to obtain more reliable data and also how to improve the composites properties to meet the applications need.

CHAPTER TWO

LITERATURE REVIEW

2.1 Acrylate polymer

2.1.1 Overview

Acrylate polymer is a group of polymers which contains vinyl group and a carboxylic acid structure. The acrylate ion has the molecular formula $CH_2{=}CHCOO^-$. **Figure 2.1** shows chemical structure for acrylate and its derivatives. **Figure 2.2** illustrated side chains present on poly (methyl methacrylate) structure.

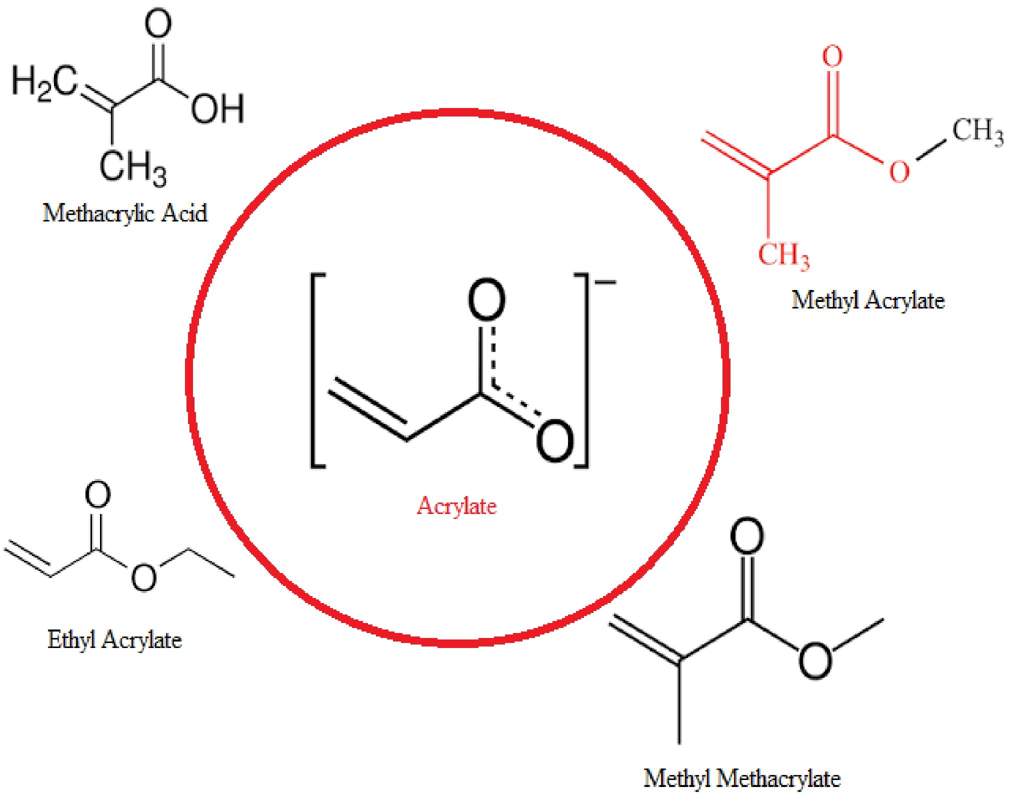


Figure 2.1: Chemical structure of acrylate and its derivatives

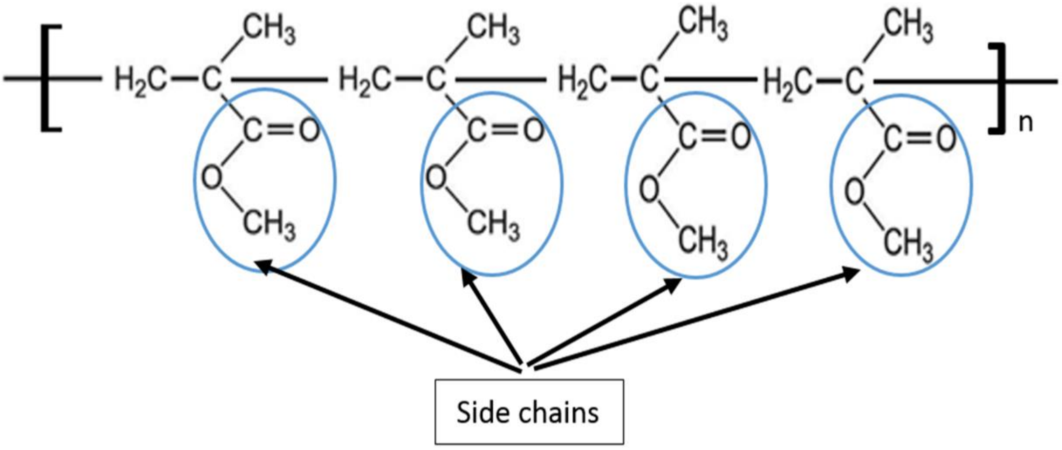


Figure 2.2: Side chains present on poly (methyl methacrylate) structure

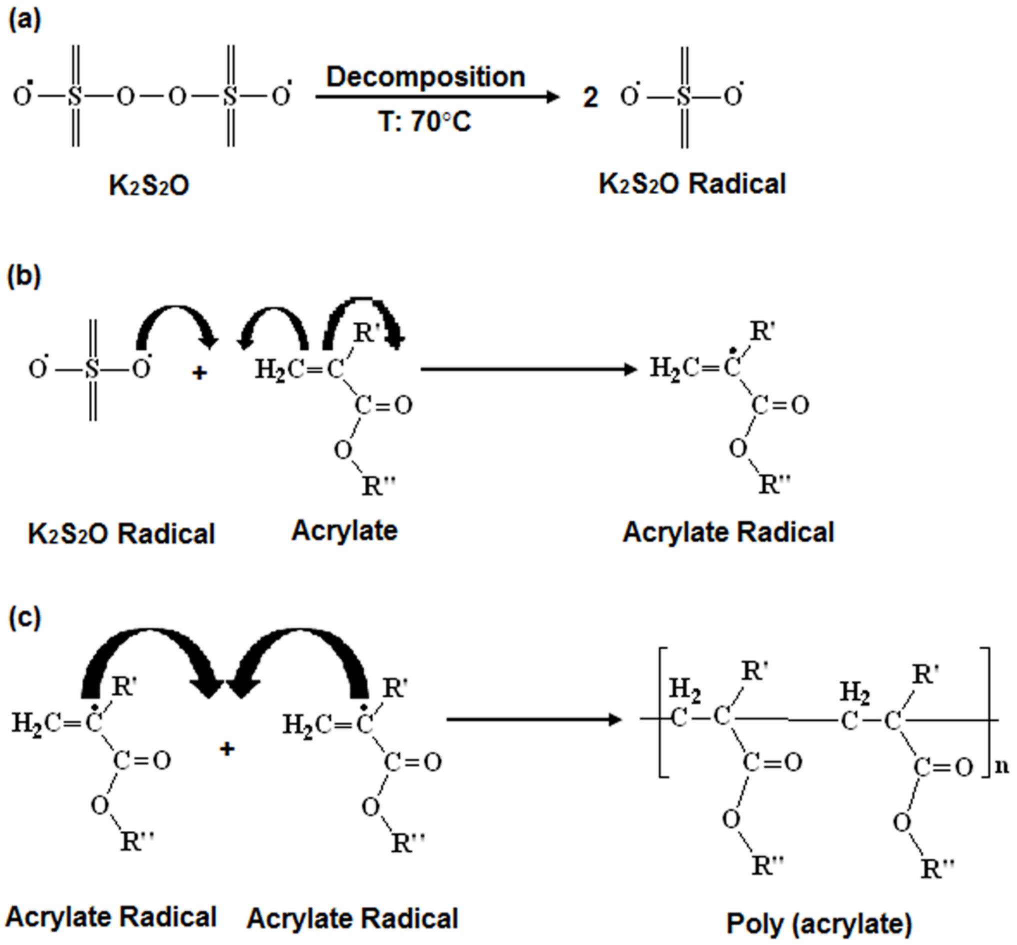


Figure 2.3: Free emulsion radical polymerization of acrylate monomer (Günaydin et al., 2005)

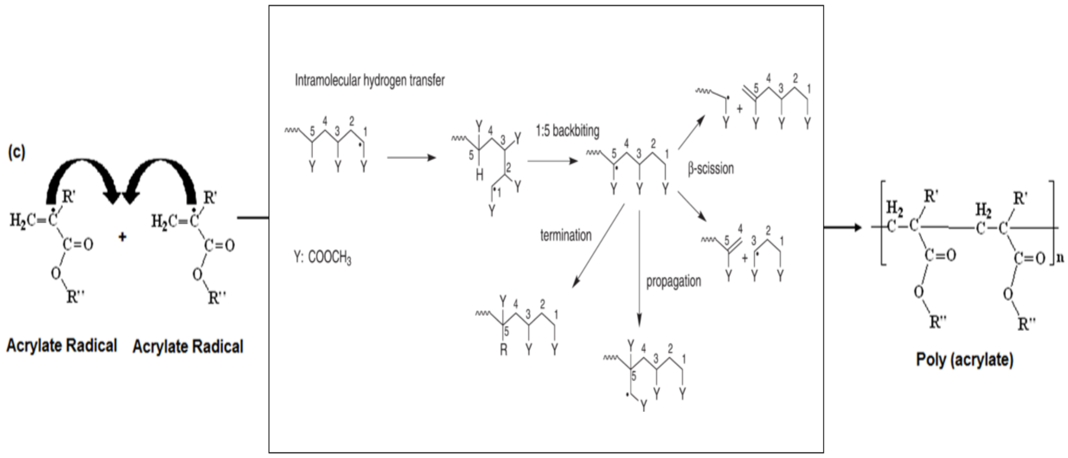


Figure 2.4: Transition phase occurs during termination and hydrogen transfer reactions (intermolecular and intramolecular) in homopolymerization of methyl acrylate (S. Liu et al., 2014)

Previous research Günaydin et al., (2005) highlighted in by **Figure 2.3** the radical polymerization of poly(acrylate) emulsion. This radical polymerization mechanism was highlighted by S. Liu et al., (2014) and **Figure 2.4** illustrated the transition phase occurs during termination and hydrogen transfer reactions (intermolecular and intramolecular) in homopolymerization of methyl acrylate.

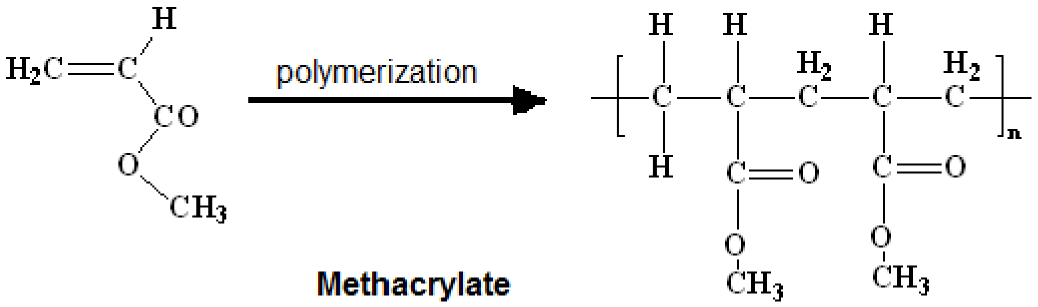


Figure 2.5: Polymerization of methacrylate into poly methacrylate (PMA) (Barner-Kowollik, 2009)

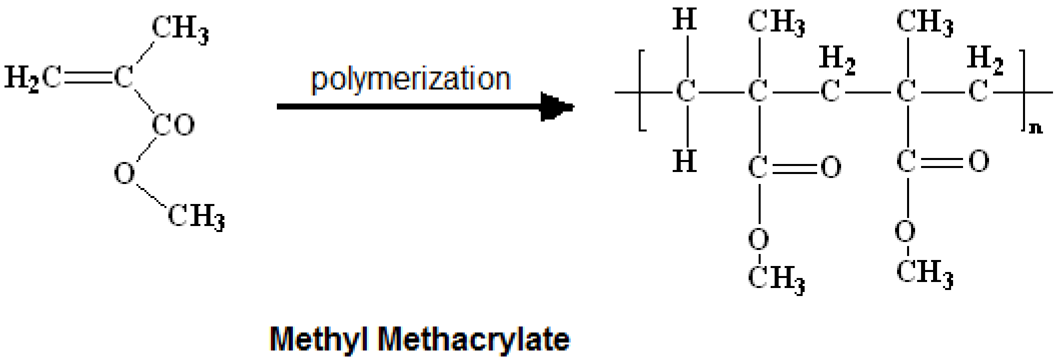


Figure 2.6: Polymerization of methyl methacrylate into polymethyl methacrylate (PMMA) (Barner-Kowollik, 2009)

Poly (acrylate) is known due to their transparency, breakage resistance and elasticity. There are several others typical acrylate monomer derives from acrylic acid, *i.e.* methacrylate, methyl methacrylate, ethyl acrylates, butyl acrylate, butyl methacrylate, hydroxyethyl methacrylate and so on. **Figure 2.5** and **Figure 2.6** shows the chemical structure from acrylate monomer to acrylate polymer.

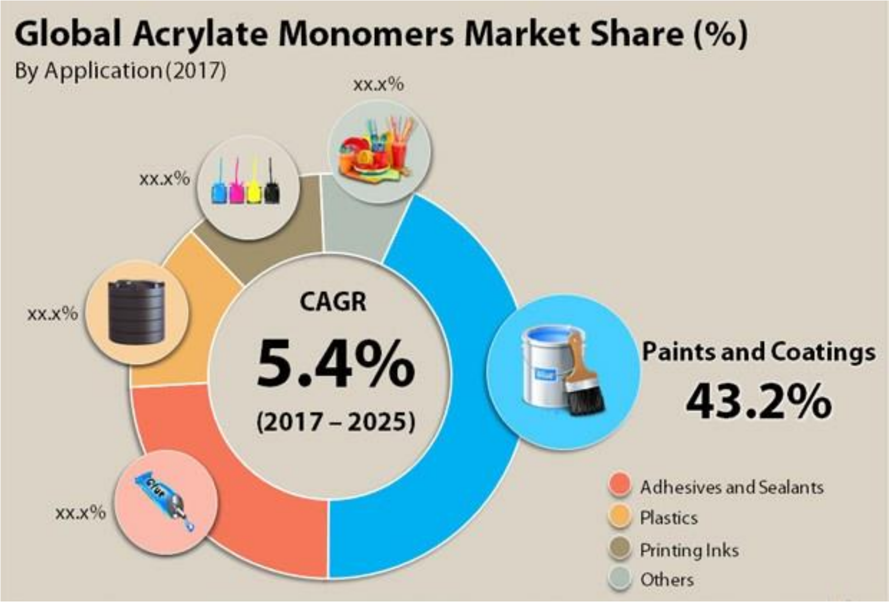


Figure 2.7: Breakdown of primary application for acrylate monomer (Research, 2017)

Nowadays, acrylate has been applied in numerous applications such as coatings, paints, automotive products, tape adhesive and high temperature resistant elastomers. **Figure 2.7** illustrates breakdown of primary application for acrylate monomer. Report studies by Transparency Market Research (2017) clarified the primary segment mostly rely on product from butyl acrylate, ethyl acrylate, methyl acrylate monomer, 2 ethyl hexyl acrylate monomer, and others. Special chemical applications usually prefer methyl acrylate monomer as their main chemical.

Moreover, methacrylate monomers have been widely used to produce dimethylaminoethylacrylate (DMAEA) which used as main monomer in manufacture water treatment flocculants. In automotive industry, acrylate elastomer is an option to fluorocarbon polymers, silicones and fluorosilicones for higher temperature application (> 156 °C). Usually, this acrylate is extensively suggested for automotive hoses, seals and dampers which require ability to perform under long term expose towards higher temperature and oils (Methylate, 2014).

In paint and coating industry, acrylate is the main ingredient for interior and exterior emulsion based paint. Furthermore, by incorporating the acrylate with solvent increase the drying rates hence give advantage for coating and printing ink application (Methylate, 2014).

Beside paint, ink, coating, acrylates are used in preparing special chemical *i.e.* pour point depressant. This product has excellent performance and extensively used as additive in oil and gas industry. Besides, this acrylate product can be formulated with various thermal properties, from sub-ambient temperature to high temperature application (Wheeler, 2013).

In terms of properties, the acrylate polymers *i.e.* poly (methacrylate) and poly (methyl methacrylate) are both tough and rubbery materials. However, poly (methyl methacrylate) is softer and elasticity compare to poly (methacrylate). Therefore, most researchers prefer acrylate either as main or co- monomer to further adjusts and improve the sample properties.

Normally, copolymerization process has been utilized as to improve existing poly (acrylate). This can be achieved by copolymerized with others monomer *i.e.* acrylonitrile, ethylene, butadiene etc. Incorporating acrylate with ethylene usually used to produce acrylate elastomers. Comparing styrene butadiene rubber (SBR) with acrylate elastomer, both have similar mechanical properties, but acrylate elastomer has good resistance to mineral oil, ultraviolet and able to withstand higher temperature.

On the basis of upstream oil and gas industry, acrylate and their derivatives have been extensively provided outstanding results as pour point depressant, fluid loss control, demulsifier, clay deflocculants etc. Due to that, this research will focus on the oilfield chemicals in order to further understand influence of proper material selection in the oil and gas industry.

2.2 Pour point depressant

2.2.1 Overview

Oil lowest temperature during cooling process under certain conditions identified as pour point. Generally, amount of wax in oil can be determined roughly thorough pour point value. Higher the pour point temperature, the more wax present in the crude oil. As the temperature reduce, wax tend to separate hence prevent the oil flow ability. Besides, waxy solids at ambient temperatures were amongst problems occurring to most pour point materials. Furthermore, many components in crude oil, specifically asphaltene, wax, gum, provide countless problems that is flow ability, corrosion, crystallization, deposition of waxy crude oil and etc., either in exploitation process or transportation of crude oil. **Figure 2.8** shows examples of pipeline corrosion and paraffin clogged occurred on pipeline inner side.

Figure 2.8: Deposition of waxy crude oil and paraffin clogged occurred on inner side of the pipeline (Yang, Zhao, et al., 2015)

As example, during crude oil refining process, high percentage of wax is removed. Due to the possibility of further wax crystallization from remaining wax in crude oil, addition of pour point depressant are chosen. PPD altered the wax crystal size as it prevents lateral crystal growth and assured the crude oil flow ability (Ismail, 2014). Moreover, addition of PPD into crude oil improved the rheological properties such as viscosity and yield stress results as the crude oil retain its fluidity even at low temperature. These results significantly reduce pumping pressure and yield stress especially after shut-down process.

In upstream industry, normal injection required was in range of 100 to 1000 ppm and the PPD were dissolved in 20 to 50 per cent in hydrocarbon solvents. Pour point depressant was injected into the hot oil to avoid formation of wax crystal. But then, the performance of pour point depressant is significantly influence by crude oil type and the additive itself (Fischer, 1993). Usually, organic solvents *i.e.* toluene and xylene are preferred due to their properties. But then, present of hydrocarbon solvent in polymeric aqueous dispersion *i.e.* ethylene vinyl acetate (EVA) tends to aggregate either gelling or separate from the solution (Norland and Kelland, 2012).

Commonly, in a stabilize solution, a solute were characterize to be in radial length of less than or equal to 1 nm. Due to that, it is possible to separate the solute from the solution under any possible circumstances. The solvent based pour point depressant did not need any agitation process *i.e.* stirring or shaking to holds its stability (Lu and Gao, 2010).

2.2.2 Acrylate as pour point depressant

In oil and gas industry, most crude oil exhibit remarkably differing physical properties influence by their broad range of hydrocarbon components. During production, this crude oil contains substantial amount of long chain alkenes or generally known as wax. This paraffin wax is insoluble and tends to precipitate below certain temperature. Various options such as stream heating, mechanical scrapping and chemical additives are available to minimize the unfavourable effects of wax on the flow properties of crude oil.

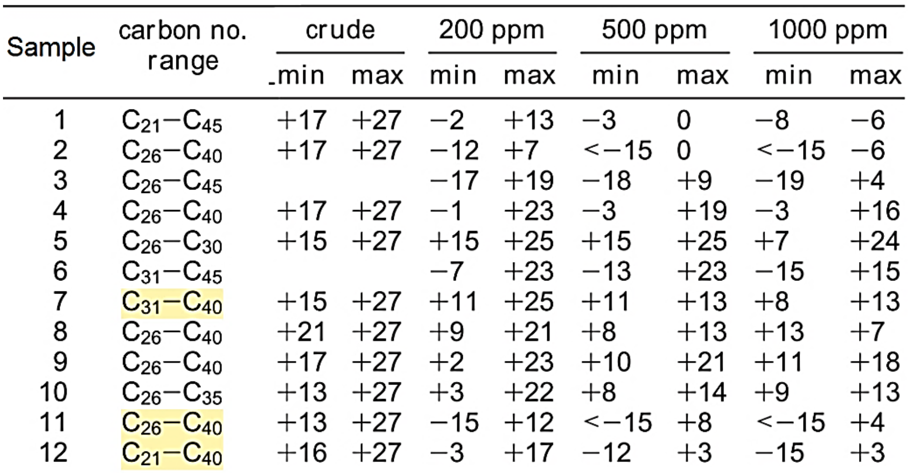
Souchik (2009) underlined that various type of acrylate polymers have been utilized to solve the wax precipitation issue. For example, poly (acrylate)s, acrylate-styrene copolymer, ethylene vinyl acetate and styrene maleic anhydride copolymers are widely commercialized product that varied from moderate to molecular weight polymer.

Pour point depressant can be separated into several categories according to their chemical structure. First category was Poly (butyl acrylate), Poly (methyl methacrylate), ethylene vinyl acetate, etc. consists long and short chains. Next category, polymer with long side chains *i.e.* poly(octadecyl acrylate-maleic anhydride). Last category is aromatic segments polymer *i.e.* poly(styrene-octadecyl maleimide) (Ren et al., 2017). However, not all these polymers showing equivalent performance even with same crude oil since as the polymer need to be compatible enough to achieved optimized result (Pedersen and Rønningsen, 2003b)**.** This PPD behaviour is due to the molecular structure of compatibility with waxy structure, and flexibility in chemical structure.

Karen S Pedersen and Rønningsen (2003b) highlighted on the impact of various alkyl chain lengths with styrene, acrylic acid and 1-vinyl- 2-pyrrolidone as copolymers via solution polymerization. As a result, the synthesized copolymer exhibit better effect on the pour point temperature compared to reference sample. **Table 2.1** shows the results for crude oil pour point data (°c) treated with different type of alkyl sample and researcher concluded that as the acrylate chain length decrease, the pour point also decrease.

Generally, pour point depressant molecules contain polar and nonpolar moieties. Vinyl acetate (VA) and maleic anhydride (MA) are example of polar moieties that could interrupt wax crystal growth and regulate thermophology of wax crystal.

Table 2.1: Study results for crude oil pour point data (°c) treated with different type of alkyl sample (Pedersen and Rønningsen, 2003b)



Sample	carbon no. range	crude		200 ppm		500 ppm		1000 ppm	
		min	max	min	max	min	max	min	max
1	$C_{21}-C_{45}$	+17	+27	−2	+13	−3	0	−8	−6
2	$C_{26}-C_{40}$	+17	+27	−12	+7	<−15	0	<−15	−6
3	$C_{26}-C_{45}$			−17	+19	−18	+9	−19	+4
4	$C_{26}-C_{40}$	+17	+27	−1	+23	−3	+19	−3	+16
5	$C_{26}-C_{30}$	+15	+27	+15	+25	+15	+25	+7	+24
6	$C_{31}-C_{45}$			−7	+23	−13	+23	−15	+15
7	$C_{31}-C_{40}$	+15	+27	+11	+25	+11	+13	+8	+13
8	$C_{26}-C_{40}$	+21	+27	+9	+21	+8	+13	+13	+7
9	$C_{26}-C_{40}$	+17	+27	+2	+23	+10	+21	+11	+18
10	$C_{26}-C_{35}$	+13	+27	+3	+22	+8	+14	+9	+13
11	$C_{26}-C_{40}$	+13	+27	−15	+12	<−15	+8	<−15	+4
12	$C_{21}-C_{40}$	+16	+27	−3	+17	−12	+3	−15	+3

Meanwhile, the nonpolar moieties usually material with long alkyl chains which interact with wax either through nucleation, adsorption or co-crystallization. According to Yang et al.(2016), adding pour point depressant into the crude oil provide tremendous changes in wax crystals hence improves the crude oil flow-ability. Furthermore, researcher concludes the optimum polar groups content provide best performance.

Research related to comb-like polymeric pour point depressant has been extensively studied due to their pour point performance and variable molecular structure. Al-Sabagh et al. (2012) and Yang et al.(2016) described branched type of acrylate such as methacrylate, methyl methacrylate, alkyl methacrylate etc. is another approaches to improve the pour point temperature. Introduction of branched acrylate will attenuated the intra-molecular force hence reduced the crystallization temperature.

2.2.3 Mechanism of PPD

Pour point depressant is produced to control the wax crystal formation hence lowering pour point and improved flow ability at low temperature. A number of researches has been done and developed various type of pour point depressant that affect the paraffin crystallization. However, most pour point depressants have constraint to perform well in different type of oil, especially crude oil. Furthermore, researchers described the analysis *i.e.* adsorption, co-crystallization, wax solubility and nucleation are widely used to propose proper mechanism.

Figure 2.9 and **Figure 2.10** illustrate the wax modification mechanism and wax crystal morphology before and after treatment. Hemant et al (2008) explained that introduce pour point depressant into the crude oil will inhibits the agglomeration hence interrupt the wax crystallization process. More specifically, Hemant et al (2008) also described the pendant chain will co-crystallize with the wax and the polar end group will disturb the crystal structure from completely form a pyramidal form.

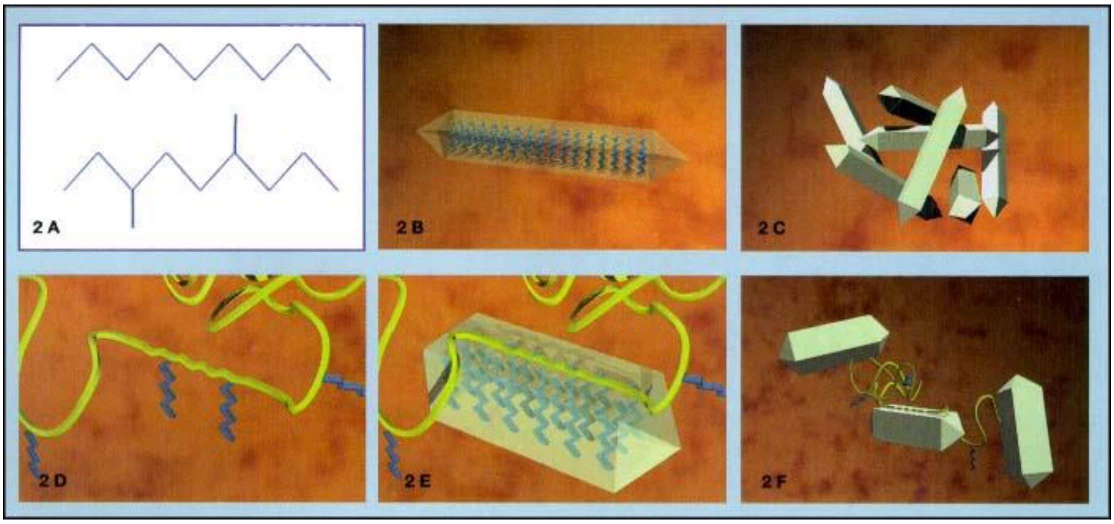


Figure 2.9: Wax modification mechanism which inhibits the agglomeration. 2A) Chemical structure of wax, 2B) Crystal shape of wax structure, 2C) Crystal structure of growing wax lattice, 2D) Polymeric Additive with wax-like components, 2E) Co-crystallization of wax and PPD, 2F) steric PPD Inhibition mechanism of wax modification (Wang et al. 1999)

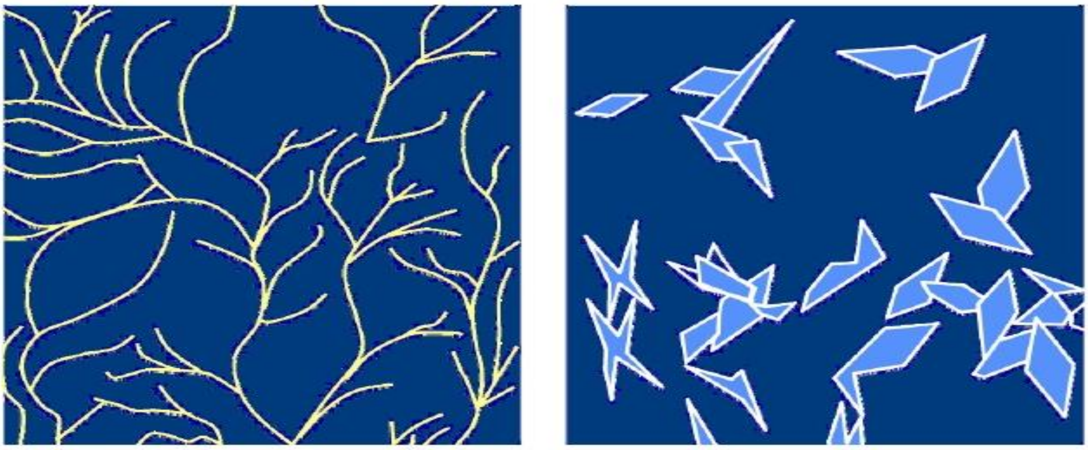

Without Pour Point Depressant
With Pour Point Depressant

Figure 2.10: Wax crystal morphology (Chevron, 2006)

But then, until now the mechanism was based only related to physical interaction between pour point depressant and crude oil. The pour point comprises plenty of resin and asphaltene which have effect on paraffin solubility. Binks et al. (2015) clarified that without proper pour point depressant, asphaltene have a tendency forming agglomerates in various solvent.

Therefore, Zhang et al. (2015) proposed prepared pour point depressant react with the crude oil to formed new macromolecule and reduce the agglomeration in solvent. This reaction improved the crude oil flow ability as it changed the wax crystallization process.

2.2.4 Pour point depressant for sub-ambient temperature

Normally, pour point depressant (PPD) are prepared by dissolved the polymeric materials in high temperature solvents to ease the processing either during injection into the down hole or transportation process through pipelines. However, these products have limitation in organic solvent solubility. Therefore, to prepared practical product, large quantity of solvents is needed (Potisek et al., 2015).

Many considerations need to be taken to prepared solvent based pour point depressant that effective in reduce the pour point below wax solubility temperature. If the PPD becomes insoluble, the polymer tends to precipitate. Hence, Binks et al. (2015) concluded that the solvent based PPD effective only within relative temperature but not all systems will certainly effective.

Researcher identified for sub-ambient temperature application, emulsion pour point depressant is more convenient in physical handling properties compare to conventional pour point depressant (Becker, 1999). Furthermore, in recent study by Admiral et al. (2016) and Rosdi et al. (2016), they highlighted that emulsion pour point depressant provide better results at optimized treat rates compare to conventional prepared pour point depressant.

Admiral et al. (2016) explained that conventional solvent based pour point depressant of acrylate polymer tends to solidified at room temperature. Therefore, it required preheating and dilution process to be completely utilized in oil and gas industry. Due to that, improvisation from conventional solvent based PPD to emulsion PPD will enhance the stability and performance of sample produced.

Numerous study related to the efficiency of emulsion pour point depressant, especially acrylate homo-polymer and ethylene vinyl acetate copolymer, compared with others additives to treat the crude oil (Admiral et al., 2016; Machado et al., 2001; Pedersen and Rønningsen, 2003a; Rosdi and Ariffin, 2016; Taraneh et al., 2008)**.** On the other hand, preparation of pour point depressant and the technology related to emulsion are less explored and discussed yet. It is crucial to explore the emulsion technology particularly for PPD as it provides thermal protection against the low temperature. This cold-flow feature of the emulsion, making the application of PPD at sub-ambient environment became plausible.

2.3 Emulsion

2.3.1 Overview

Common industries such as oil, paint, agrochemical, food and pharmaceutical, the emulsion produced either during product preparation or final product. Emulsion and foams are closely related. Foams produced through dispersion of gas in liquid or solid while emulsion is known as fine dispersion of liquid droplets in another non-soluble liquid. **Figure 2.11** illustrates basic system consists of oil, water and surfactants that forms a single thermodynamically stable emulsion.

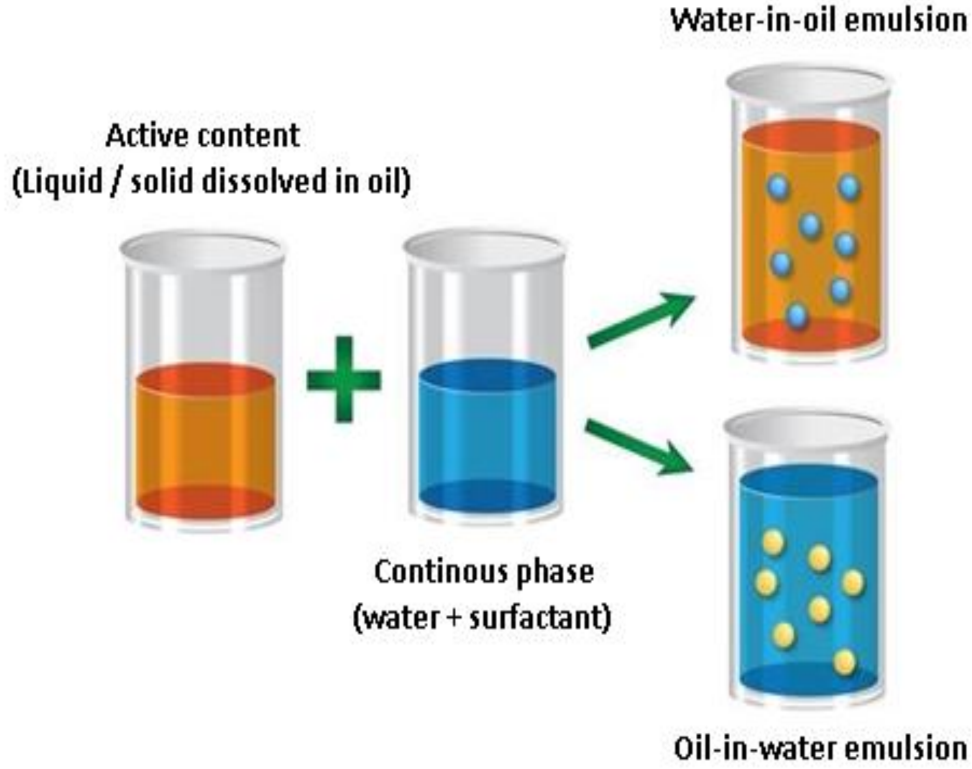


Figure 2.11: Basic system of oil, water and surfactants that forms emulsion (Croda, 2017)

Generally, it was difficult to mix oil and water due to the repel force and difference in electrical charges of each molecules. Water known as polar molecule and tends to attract to each other. While, the oil molecule is non-polar due to that