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UNIVERSITI TEKNOLOGI PETRONAS

SYNTHESIS, CHARACTERIZATION AND EVALUATION OF POUR POINT DEPRESSANTS FOR MALAYSIAN WAXY CRUDES

by

SAPIAH BINTI ALI

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SYNTHESIS, CHARACTERIZATION AND EVALUATION OF POUR POINT DEPRESSANTS FOR MALAYSIAN WAXY CRUDES

by

SAPIAH BINTI ALI

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DECLARATION OF THESIS

Title of thesis: SYNTHESIS, CHARACTERIZATION AND EVALUATION OF POUR POINT DEPRESSANTS FOR MALAYSIAN WAXY CRUDES

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DEDICATIONS

To my beloved husband and my dearest children

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"In the name of Allah, the most Beneficent, the most Merciful"

Alhamdulillah. All praises are to Allah who has made this work possible and a successful one.

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ABSTRACT

Waxy crudes production from the offshore is plagued with flow assurance challenges due to seabed low temperatures and high pour point and WAT of the waxy crudes. Studies on the rheological properties of waxy crude oil are important in order to synthesize an optimal PPD for different waxy crude oil.

Five polymeric PPDs have been synthesized, characterized and evaluated against two Malaysian waxy crudes possessing high pour point and WAT. A family of anhydride copolymers was synthesized by copolymerization acrylates with maleic anhydride, which were then reacted with hexadecylamine to produce the polymeric PPDs called Poly (n-alkyl acrylates-co-N-hexadecylmaleimide).

The polymeric PPDs were characterized by FTIR-ATR and SEC to determine their functional groups and molecular weights, respectively. The performance of the polymeric PPDs was evaluated for their reduction of pour point, WAT, viscosity and yield stress of two waxy crudes. WAT has been tested using CPM, while the viscosity and yield stress properties were analyzed using Haake Rheostress 6000. The polymeric PPDs influence on the wax morphologies of the waxy crudes was studied using an AFM.

The synthesized PPD has reduced the pour point temperature of Crude A2 by 6°C (12.5% reduction) at 500 ppm and Crude A6 by 12°C (21% reduction) at 1000 ppm dosage. It has reduced the viscosities of Crudes A2 and A6 at 45°C and $500 s^{-1}$ by 35% and 37%, respectively. The PPD has also reduced the yield stress of Crude A2 at a reduction of 26% from 109 Pa to 81 Pa. The total crystal at 45^{o}C was drastically reduced for the PPD treated crudes; however, WAT was only marginally influenced by the PPDs.

The flow assurance is overall improved when the pour point is depressed as well as when the viscosity and yield stress are reduced.

ABSTRAK

Penghasilan minyak mentah berlilin dari luar pesisir disertai dengan cabaran kebolehan aliran minyak disebabkan oleh suhu dasar laut yang rendah dan suhu takat tuang serta suhu penampilan lilinnya yang tinggi. Kajian ke atas sifat-sifat reologi minyak mentah berlilin adalah penting untuk mensintesis PPD yang optimum bagi minyak mentah berlilin yang berlainan.

Lima PPDs polimer telah disintesis, diciri dan dinilai ke atas dua minyak mentah berlilin Malaysia dengan suhu takat tuang dan suhu penampilan lilin yang sangat tinggi. Kopolimer anhydride telah disintesis dengan pengkopolimerisasi akrilat daripada lima alkyls dengan maleic anhydride yang kemudian bertindak balas dengan hexadecylamine untuk menghasilkan Poli (n-alkil akrilat bersama-N-hexadecylmaleimide).

PPD polimer dicirikan dengan FTIR-ATR untuk melihat kumpulan berfungsi dan GPC untuk menentukan berat molekul mereka. Prestasi PPDs polimer telah dinilai untuk melihat pengurangan suhu takat tuang, WAT, kelikatan dan tekanan hasil minyak mentah berlilin. WAT telah diuji menggunakan CPM; manakala analisis kelikatan dan tekanan hasil telah diuji menggunakan Haake Rheostress 6000. Pengaruh PPD polimer ke atas morfologi lilin minyak mentah berlilin telah dikaji menggunakan AFM.

PPD yang disintesis telah mengurangkan suhu takat tuang Crude A2 sebanyak 6 °C (12.5%) pada dos 500ppm dan Crude A6 sebanyak 12 °C (21%) pada dos 1000ppm. Ia telah mengurangkan kelikatan Crude A2 dan Crude A6 masing-masing sebanyak 35% dan 37%, pada 45° C dengan kadar ricih 500s-1. PPD juga telah mengurangkan tegasan alah Crude A2 sebanyak 26%, dari 109 Pa hingga 81 Pa. Jumlah kristal telah dikurangkan dengan drastik pada suhu 45°C tetapi WAT tidak berubah dengan penambahan PPD.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

WAT	Wax appearance temperature
PPDs	Pour point depressants
FTIR-ATR	Fourier Transform Infrared - Attenuated Total Reflectance
GPC	Gel permeation chromatography
SEC	Size exclusion chromatography
EVA	Ethylene-vinyl acetate
IR	Infra-red
MS	Mass spectroscopy
API	American Petroleum Institute
ASTM	American Standard Testing Method
SG	Specific gravity
DSC	Differential scanning calorimetry
CPM	Cross polar microscopy
UOP	Universal Oil Products
NHI	n-heptane insoluble
HTGC	High temperature gas chromatography
Mw	Molecular weight
THF	Tetrahydrofuran
PMO	Peninsular Malaysia Operation
AFM	Atomic Force Microscopy
NMP	N-methyl-2-pyrrolidinone
PNA	Paraffins, Napthenes, Aromatics
SARA	Saturates, Aromatics, Resins, Asphaltenes

CHAPTER 1

INTRODUCTION

1.1 Background

Crude oils from different fields vary widely in appearance, viscosity, wax contents, pour point and WAT. This diversity causes them to possess differing physicochemical properties. The complex nature of crude oil creates many problems during its transportation especially in offshore production. Live crude gradually becomes viscous and sluggish at lower temperatures when it has to be transported over long distances through the pipelines. The presence of wax crystals in the crude is a major problem which restricts the oil to move freely.

WAT is the point at which wax crystals begin to precipitate out of oil under specified cooling conditions. At WAT the paraffins crystallize out of the solution and start to build a 3D network with a complex morphology. The portion of solids needed to build a stable structure is very low, in the range of 2% w/w (Kane *et al.,* 2003). Generated network entraps the rest of the fluid inside and so-called wax-oil gel is produced (Singh *et al.,* 2001). The gelling significantly increases the fluid viscosity and changes the rheological behaviour from Newtonian to non-Newtonian (Singh *et al.,* 1999).

During regular pipeline flow, the paraffin structure is usually weak and might be disturbed by an ordinary flow itself. More problems occur during the pipeline shutdown. In such a case, solids build a compact network across the whole pipeline cross section area and additional energy (yield pressure) is needed to restart the flow satisfactorily (Kane *et al.,* 2003).

The presence of paraffin waxes in crude oil causes serious problems to the production, transportation and refinery operations. Crude oil containing high amount of wax exhibit a high pour point and non-Newtonian viscosity behavior below WAT (Deshmukh and Bharambe, 2007). The pour point of crude oil is the lowest temperature at which crude oil stops flowing. When the crude reaches the pour point, the paraffin in the crude crystallizes and forms a matrix of wax crystals. This wax-crystal matrix holds the bulk of the liquid portion of the crude within it and prevents the liquid from flowing. Anything that disrupts the formation or alter the properties of the wax-crystal matrix, such as PPDs, will affect the pour point (Manka *et al.,* 2001).

Wax crystallizes out of the liquid hydrocarbon solution below WAT and causes the gelation of oil and a dramatic increase in the viscosity (Li and Zhang, 2005). As temperature decreases, the abrupt rise in the crude oil viscosity depends upon the quantity as well as the type of wax present in it.

In the production, storage and transportation of waxy crude oils, it is important that the oil is kept above its natural pour points. Production chemicals known as flow modifiers, crystal modifiers, viscosity improvers and pour point depressants are utilized to lower the apparent viscosities, yield points and pour points of crude oils (Son *et al.,* 1993).

In order to counteract the problems caused by n-paraffin deposition, several options are available through various mechanical, thermal and chemical means (Bilkler and Mc Dougall, 1969; Uhde and Kopp, 1971).

Pigging is a mechanical removal process, which is often carried out at regular intervals in conjunction with continuous wax inhibitor treatments to reduce the rate of wax deposition and soften the deposited waxes. The success of mechanical pigging is highly dependent upon the properties of the debris in the pipeline, the pig design, and the transport capacity of the carrier fluid in the line (Wang *et al.,* 2003).

When paraffin waxes block the inside of the pipe, an additional process is needed to remove it, which then leads to a reduced production efficiency. To maintain the inner-wall temperature above the paraffin-formation point, the heat loss from the pipe wall must be minimized.

In most cases, paraffin problems can be resolved efficiently and economically with chemical products (Dobbs *et al.,* 1999). Paraffin precipitation may be treated chemically with solvents, dispersants and wax modifiers. A preferred option would be to use wax modifier additives, commonly known as PPDs. These compounds do not dissolve, disperse or remove paraffin that has already been deposited. They are applied in either continuous or squeeze-type treatment to restrict the crystal size and shape of precipitated paraffin which helps to prevent re-agglomeration of paraffin crystals (Svedgoff *et al.,* 1984 and Wong *et al.,* 1999).

Treatment of waxy crudes with PPDs offers a solution to high pour point problems. However, a major uncertainty with the chemical additive treatment for reducing the pour point is that waxy crudes only show a limited response to the additives. Moreover, the exact mechanism of pour point reduction, while often hypothesized, still remains unknown.

A standard method of PPDs selection, formulation techniques and processes are not readily available with respect to the offshore production of waxy crude oils with high pour points. Development of an optimum PPDs according to the nature of specific crude is highly desirable. Because of the diverse nature of crudes and production conditions there is no single PPD that can be generalized to enhance flow-assurance.

Wax crystal morphology and structure along with the composition of a crude oil play a dominant role in the rheological properties when the oil temperature is below the WAT. To quantify the relation between rheological behaviors and wax crystal morphology a better understanding of the involved mechanism is required (Zhang *et al.,* 2008).

The present work provides laboratory data to illustrate that the polymeric PPDs can improve the flow assurance by depressing the pour point, reducing the viscosity and decreasing the yield stress of the treated crudes. The yield stress was simply defined as the minimum stress required in producing a shear flow (Chang, 1998).

1.2 Problem Statement

A number of existing and future fields to be developed in the Malay basin possess waxy crudes with high WAT and high pour point. Flow-assurance of such kind of crude oils especially from offshore fields poses a great challenge to operations. At present, the enhancement of flow-assurance of waxy crudes from offshore fields assisted by PPDs is not fully explored. Precise information is required in order to make a correct decision on the flow-assurance feasibility development. Due to the unique properties of every crude oil and the specificity of the PPD, there is a need for an understanding of the performance of wax control chemicals at the molecular level as a route to simplify our understanding and present a general approach to managing waxy crudes.

1.3 Objectives

The aim of this study is to synthesize polymeric PPDs, characterize and evaluate their performance to modify the wax crystals and to reduce the pour point and rheological properties of waxy crudes possessing high WAT and pour points. In order to achieve this aim, the proposed research was subdivided into the following objectives:

1. To fully characterize the high waxy crudes possessing high WAT and pour points

2. To synthesize, characterize and evaluate the polymeric PPDs to treat the waxy crude oil with high WAT and pour points.

3. To evaluate the commercially available PPDs for the performance comparison against the synthesized PPDs.

1.5 Thesis Organization

The primary objective of this study was to develop a chemical formulation to enhance the flow assurance of waxy crudes. The PPDs were evaluated for their performance in depressing the pour point and reducing the viscosity and yield stress of the waxy crudes.

This thesis is composed of five chapters including introduction, literature review, experimental works, results and discussions, and conclusions and recommendations.

Chapter 1 provides a brief introduction to crude characteristics, flow assurance problem and wax control additive characteristics.

Chapter 2 reviews the background literature that is relevant to the paraffin wax deposition and the development of pour point depressants for crude oils.

Chapter 3 deals with the experimental works including characterization of waxy crudes, synthesis and characterization of synthesized PPDs, and evaluation of the synthesized and commercially available PPDs.

Chapter 4 details the results obtained from the study and deals with the discussion of the characterization and evaluation of the synthesized PPDs and the comparison study of synthesized PPDs against the commercially available PPDs.

Chapter 5 summarizes the main conclusions of the thesis and provides recommendations for further work.

CHAPTER 2

LITERATURE REVIEW

This chapter reviews the background literature that is relevant to the paraffin wax deposition and the development of pour point depressants for crude oils. Section 2.1 covers the composition of crude oils and waxes overview which includes the nature of crude oil and wax deposit; wax precipitation and deposition; wax crystallization mechanism; and crude oil and wax testing. Section 2.2 covers the works done by other researchers in the development of PPDs and testing of PPDs.

2.1 Composition of Crude Oils and Waxes

Crude oils produced from the formations are transported and processed at low temperatures where solid wax particles may precipitate. These solid particles cause additional pressure drop in the production tubing and pipeline causing the reduction of the effective flow area through the pipelines, which can ultimately lead to total blockage as shown in Figure 2.1.

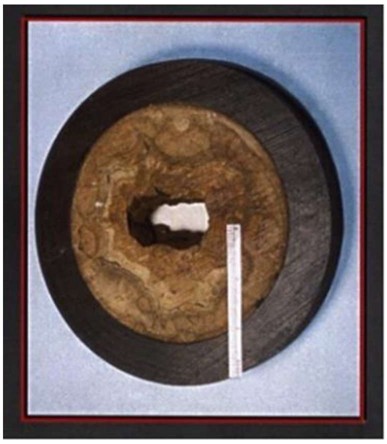


Figure 2.1: A pipeline blocked with wax deposit (Singh *et al.*, 2001)

Wax precipitation within the pipelines at and below WAT can lead to gelling that inhibits flow by causing significant non-Newtonian behaviour and increasing effective viscosities as the temperature of a waxy crude oil approaches its pour point (Pedersen and Rønningsen, 2003). Alternatively, when the temperature of the pipeline wall is below the WAT, there will be an increased risk of deposition of a layer of paraffin molecules that can grow over time hence, constricting flow (Azevedo and Teixeira, 2003). This is especially problematic for pipelines in deep-sea environments.

Wax deposition, a function of a number of parameters including crude oil composition, temperature, pressure and fluid mechanics, can occur at sufficiently low temperatures where the liquid wax particles precipitate out of solution (Machado *et. al.,* 2001, Taraneh *et al.,* 2008).

Since WAT is sensitive to the waxy crude composition, it is useful to briefly review the compositions of petroleum fluids and waxes. In general, petroleum fluids can be classified into four major fractions denoted as saturates, aromatics, resins, and asphaltenes (SARA). Saturates are non-polar and consist of normal alkanes (n-paraffins), branched alkanes (iso-paraffins) and cyclo-alkanes (naphthenes). Saturates are the largest single source of hydrocarbon or petroleum waxes, which are generally classified as paraffin wax, microcrystalline wax and/or petrolatum (Warth, 1956). Of these, the paraffin wax is the major constituent of most solid deposits from crude oils. (Hammami *et al.,* 2003).

2.1.1 Nature of Crude Oil

Crude oil is found in the underground deposits throughout the world and contains compounds of hydrocarbons as well as sulphur and nitrogen. The exact molecular composition varies widely from formation to formation but the proportion of chemical elements varies over fairly narrow limits. Its elemental composition is fairly constant with 83-87% carbon, 10-14% hydrogen, 0.1-2% nitrogen, 0.05-1.5% oxygen and 0.05-6% sulphur (Speight, 1991).

Crude oils contain mixtures of light and heavy hydrocarbons that can be classified as paraffins, naphthenes and aromatics as heavy as C60 or C70 in addition to polars and asphaltenes (Mazee, 1973). The distribution of the different types of hydrocarbons in petroleum also varies considerably from one crude oil reservoir to another which means that the properties of the various crude oils are quite different

This solubility depends on pressure, temperature and composition of crude oils. The presence of light ends increase, the solubility of wax in crude oil. Asphaltene acts as inhibitor for wax formation (Misra *et al.,* 1995).

Crude oils can be categorized according to their flow ability; firstly the light crude oil with good flow ability, and secondly, crude oil with high pour-point or high viscosity with low flow ability. Crude oils with wax contents above 5% are usually considered as waxy crude oil (Zhang and Liu, 2008). A majority of crude oils that are > 20° API contain a significant portion of paraffin or n-alkane components. Paraffins > C20 are the components that commonly cause deposition or congealing oil in crude oil systems (Campbell *et. al.,* 2003).

The study by Shedid and Zekri, 2002 indicated that crude oil of higher sulfur concentrations has higher viscosity than that one of lower concentration. Sulfur compounds are considered as the most important non-hydrocarbons in crude oils, because of their corrosive nature, their deleterious effects on petroleum products, their tendency to plug porous medium, which may impair formation productivity, their effect on oxidation characteristics, and their disagreeable odor.

2.1.2 Nature of Wax Deposit

Paraffin waxes are essentially mixtures of long-chain n-paraffins, ranging from C15 to C75+ (Allen *et al.,* 1989, Srivastava *et al.,* 1993; Hunt, 1996).

Two types of wax are commonly encountered in crude oils. The first is the macrocrystalline wax composed of mainly straight-chain paraffins (*n*-alkanes) with varying chain length (about C20–C50). The second is the microcrystalline or amorphous waxes containing high portion of isoparafins (cycloalkanes) and naphthenes with a molecular weight ranges from C30 to C60. The presence of these solid particles (Figure 2.2) causes a change in the flow behavior of crude oil from Newtonian to non-Newtonian (Ronningsen *et al.*, 1991), thus, resulting in a marked increase in crude oil viscosity and hence additional pressure drop (Mc Claflin *et al.*, 1983, and Agarwal *et al.*, 1990).

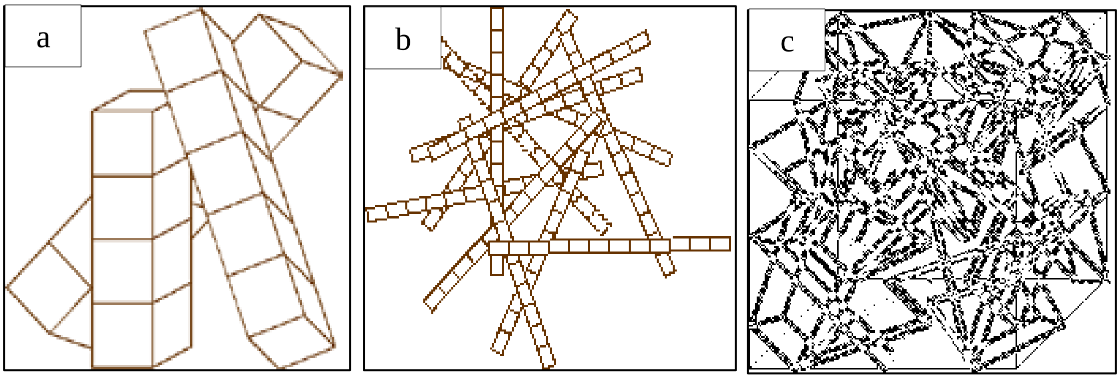


Figure 2.2: Network of wax (Mansoori *et. al.*, 1996) a) Macrocrystalline, b) Microcrystalline, c) Crystal deposit

Asphaltenes and residual oil components often co-precipitate with the paraffin waxes and result in varying appearance (colour) and texture to the precipitated solids. (Hammami *et al.,* 2003). At temperatures below WAT, wax precipitates out from the crude oil gradually with decreasing temperature (Figure 2.3), and the crude oil exhibits a non-Newtonian behaviour.

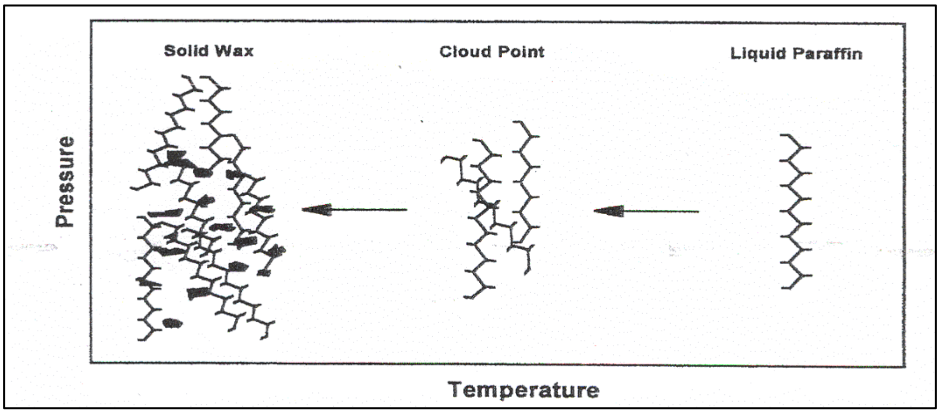


Figure 2.3: Wax precipitation (Mansoori *et al.*, 1996)

The depositions of paraffin or wax are influenced by temperature reduction of the oil, loss of volatile components that act as solvents, foreign matter that makes a nucleus for deposition and surface conditions of the equipment (Dobbs *et al.,* 1999). The type of wax is a function of the carbon atoms in the molecule. The melting temperature increases with the carbon number. Generally, wax components in the carbon number range of C12 to C25 are classified as soft and those in the C25 to C50+ range as hard. When the precipitated amount of wax is 2 - 4% of the total mass of the crude oil, the crude oil becomes a gel and loses its flow ability (Li *et al.,* 2005)

2.1.3 Wax Depositions Mechanism

The waxes in crude oils are paraffinic in nature and vary in amount and molecular weight distribution. When waxy crudes are cooled down, the paraffinic wax starts to crystallize in the form of thin plates, needles or malcrystals, with the needles being the most problematic. As wax components come out of solution, the needles compact into a three-dimensional network. Plates curl on their edges forming hollow needles which can then network (Son *et al.,* 1993).

The solubility of n-paraffins in organic solvents drastically decreases as a function of temperature (Singh *et al.,* 1999). Therefore, as the crude oil progresses through the pipeline, the crude will continue to become cooler and it becomes possible that some of the n-alkanes present in the crude will reach their solubility limit.

Once the n-alkanes reach their solubility limit, they will precipitate out in the form of solid crystals. For the temperatures typically seen in subsea oil pipelines, these precipitated wax crystals will come from n-alkanes with a carbon number of approximately 18 or higher (Anderson *et al.,* 2001, Bhat and Mehrotra, 2008). If this precipitation occurs close enough to the pipeline wall, deposition on the pipeline wall can result.

Investigations in the wax deposition mechanisms have been ongoing for decades by researchers such as Burger *et al.,* 1981 and Leiroz and Azevedo, 2005. Numerous mechanisms including molecular diffusion, shear dispersion, Brownian diffusion and gravity settling have been proposed to explain deposition in subsea oil pipelines, but it is generally accepted that deposition follows molecular diffusion (Singh *et al.*, 2000).

In a pioneering work, Burger *et al.*, 1981 found that in most models of wax deposition, molecular diffusion is treated as the dominant mechanism, and it is also argued that experimental evidence suggests that gravity settling and shear dispersion play no significant role in wax deposition.

2.1.3.1 Molecular diffusion mechanism

At the onset of cooling, the temperature at the pipe centre is higher than that at the pipe wall. For example, in a typical subsea pipeline, oil from the reservoir flows at about 80ºC while the pipe walls are at sea bed temperature of about 5ºC. This radial temperature gradient gives rise to a radial gradient of wax concentration in the oil where the concentration in the centre of the pipe is higher than that at the pipe wall where wax particles are precipitating and depositing on the wall. This concentration gradient in turn leads to a radial transport of wax molecules towards the wall by molecular diffusion.

2.1.3.2 Brownian diffusion mechanism

Brownian diffusion is the random displacement of wax particles suspended in the bulk oil due to collision with the thermally agitated oil molecules. The movement of these particles is preferentially from the hotter regions to the colder regions with less agitation, thus resulting in a concentration gradient across the fluid.

2.1.3.3 Shear Dispersion

During laminar flow in a pipe, velocity is maximum at the center of the pipe and minimum at the wall where shear stress is maximum. This velocity profile gradient induces an angular velocity to the solid particles in the flowing fluid driving them towards the wall. This deposition mechanism suggests that flow is required for deposition and theoretically no heat flux between the pipe and the environment is required to sustain deposition.

2.1.3.4 Gravity Settling

It seems logical that since there is a difference between the densities of wax particles and the oil solvent, there should be some effect of gravity driving the denser particles from the solution to the bottom. However, various researchers have concluded that this effect is negligible. Burger *et al.,* 1981 investigated the effect of this mechanism by studying wax deposition in vertical and horizontal tubes under dynamic and quiescent conditions and concluded that this effect was not significant. Similar results were obtained by Leiroz and Azevedo, 2003. Generally in literature, not much information is available about this mechanism and its significance in wax deposition.

2.1.4 Crude Oil and Wax Testing

Crude oil samples have been tested using a variety of techniques. Paraffin deposition, viscosity, cloud point, pour point, yield values, wax extraction and GLC tests have been conducted in order to characterize the crude oil samples. The effects of various chemical additives were then analyzed using the same tests. The effective paraffin inhibitors not only reduced the quantity of wax deposited, but dramatic shifts in molecular weight range and configuration were also apparent.

The combination of pour point, viscosity and yield value data has been determined to effectively describe a crude oil's rheological properties with and without chemical additives.

The use of analytical instruments such as GLC, mass spec and GPC has led to information on the chemical composition and distribution of the high molecular weight fractions contained in the crude oil.

2.2 Development of Pour Point Depressants

In order to counteract the problems caused by n-paraffin deposition, several options are available, including mechanical, thermal and chemical means (Bilkler *et al.,* 1969; Uhde and Kopp, 1971). In most cases, paraffin problems can be resolved efficiently and economically with chemical products (Dobbs *et al.*, 1999). Paraffin precipitation may be treated chemically with solvents, dispersants and inhibitors (wax modifiers).

2.2.1 PPDs for Wax Removal and Inhibition

Several methods have been presented to the industry for coping with wax related problems (Hunt, 1996; Bernadiner, 1993; Ferworn, 1997). These methods fall into three different categories, namely thermal, mechanical, and chemical.

A variety of mechanical, thermal and chemical treatments have evolved over the years to alleviate the problems associated with deposition and pumping. If the wax content of the crude oil is low to moderate (0-10%), these problems are periodic in nature and are handled on an “as need basis”, whereas with wax contents of above 10% these crudes experience severe deposition and flow problems necessitating constant treatment to ensure continued production (Matlach *et al.,* 1983).

PPDs are generally used to lower the pour point, viscosity and yield stress of crude oil. Pretreatment of waxy crudes with PPDs can minimize these problems to a certain extent and has become an emerging technology for the offshore production of waxy crudes and is being widely used (Zettlitzer, 2000; Zhang *et al.*, 2001). The continuous addition of polymeric inhibitors is considered as an attractive technological alternative.

There are many kinds of polymers that are used as PPDs to influence the behavior of the paraffin crystals formation (Bunger *et al.,* 1981, Garcia *et al.,* 2000 and Al Sabagh *et al.,* 2002). Some polymeric compounds used as PPDs are poly alkyl acrylates and methacrylate copolymers, alkyl esters of styrene maleic anhydride copolymers, alkyl actylate-alkyl maleate copolymers, ethylene-vinyl acetate copolymers (EVA) and alkyl fumarate-vinyl acetate copolymers. They are typically polymers that contain a long alkane chain to interact with the wax and side (typically polar) groups to limit co crystallization and gelation (Kuzmic *et al.*, 2008).

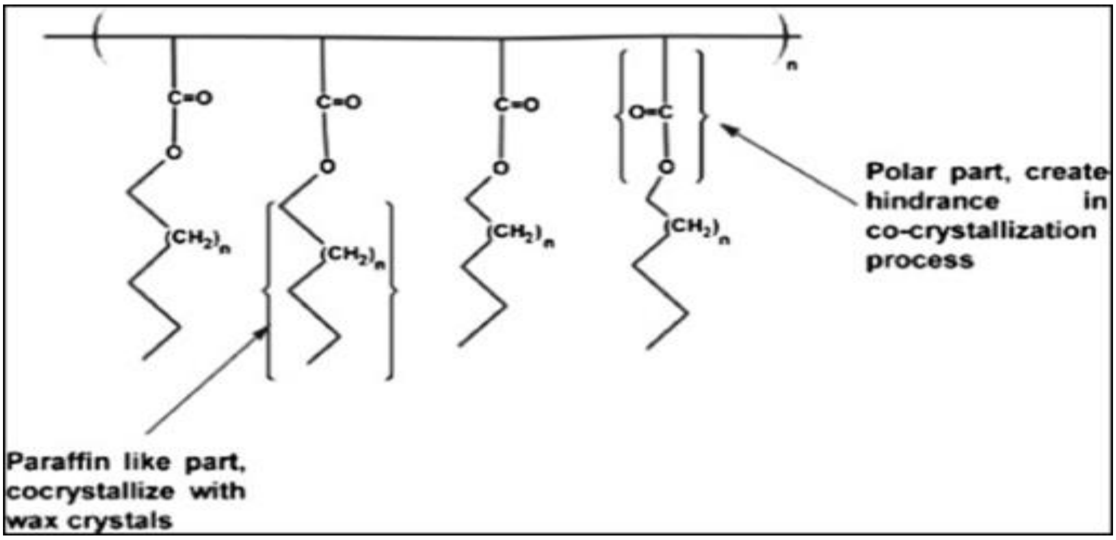


Figure 2.4: Characteristic structure of a comb polymer PPD (Soni *et al.*, 2008).

PPDs, also known as crystal modifiers, work by co-crystallizing with the wax crystals. The change in the crystal shape diminishes the ability of waxy aggregates to interlock, resulting in the lowering of the pour point of the crude significantly.

Although a wide number of polymers can be used as wax inhibitors, their efficiency is extremely sensitive to both the composition of the oil and the concentration of the additive added (Garcia *et al.*, 2001). Some additives that effectively reduced the pour point for one group of oils either minimally impacted or in some cases increased the pour point for the other group oils. The best inhibitor for one crude oil could be the worst inhibitor for another crude oil (Dong *et al.*, 2001).

2.2.2 Synthesis, characterization and evaluation of PPDs

There are various ways of designing a chemical that will interfere with the wax nucleation and crystallization process. Three main classes of wax inhibitors and PPDs are ethylene polymers and copolymers, comb polymers and miscellaneous branched polymers with long alkyl groups (Kelland, 2009).

Comb polymers are generally regarded as the most effective class of wax inhibitors (Singhal *et al.,* 1991). They are usually made from one of two classes of monomers, (meth) acrylic acid, or maleic anhydride or both.

A study by Soni *et al.,* 2006 dealt with the synthesis of copolymers of maleic anhydride and esters of n-alkyl alcohols with oleic acid and methacrylic acid. The resulted copolymers were esterified with two moles of fatty alcohol. They were characterized by IR spectroscopy and their molecular weights were determined by GPC. These polymeric diesters with pendant fatty chains were evaluated for their efficiency as pour point depressants and flow improvers on crude oil from Gandhar oil field (Gujarat, India). Different doses of synthesized polymeric additives were examined at different temperatures with the crude oil to evaluate pour point depressants and to study the dependence of shear rate on its shear stress and viscosity.

Hafiz *et al.,* 2007 has developed new crystal modifier surfactants by esterification of hexa-triethanolamine with oleic acid to prepare mono, di, and tri-esters. The synthesized esters were confirmed by IR spectroscopy and the molecular weight of the major compound in the reaction mixture was determined by MS analysis. The synthesized esters were evaluated as flow improver and PPD. Hexa-triethanolamine mono-oleate was most efficient for crude oil (I), and hexa-triethanolamine tri−oleate was most efficient for crude oil (II).

Deshmukh and Bharambe, 2007 have synthesized five flow improvers to study rheological properties of waxy crude oil. Anhydride copolymers were prepared making use of the copolymerization of acrylates of different alkyls with maleic anhydride and the Poly (n-alkyl acrylates-co-Nhexadecylmaleimide) was prepared by the reaction of copolymer with hexadecylamine. The prepared polymeric additives shows dual function both as wax dispersants and flow improvers and all of them acts as good pour point depressants.

Taraneh *et al.,* 2008 has evaluated the influence of EVA with different ranges of molecular weight, as flow improver on the viscosity and pour point of five Iranian waxy crude oils. Five types of Iranian waxy crude oil were selected based on their similar wax but different asphaltene contents. The rheological behavior of these crude oils, with middle range API gravity, in the absence/presence of flow improver was studied. The results indicated that the performance of flow improver was dependent on the molecular weight and the asphaltene content.

Wu *et al.,* 2012 has investigated the influence of structure variables of polymeric additives on the pour-point depression and rheological behavior of waxy crude oil by designing and synthesizing the maleic anhydride co-polymer and its derivatives with different polar and/or aromatic pendant chains. All prepared additives were characterized by FTIR and GPC; and evaluated on Changqing crude oil with low asphaltene content. The results showed that all four polymeric additives exhibited good efficiency as flow improvers for Changqing crude oil. The reduction of pour-point and rheological parameters after additive addition was largely related to the polymer structure. The polymer containing aromatic units showed the best performance, which could depress the pour point by 19 °C and decrease the yield stress as well as viscosity to a large extent.

Table 2.1 summarizes the related works as discussed above by other researchers on the synthesis of PPDs to tackle the flow assurances problems in the production of waxy crudes.

Table 2.1: Related works on PPDs synthesis for waxy crudes

Authors	Work	Findings
Soni *et al.*, 2006	• Synthesis of copolymers of maleic anhydride and esters of n-alkyl alcohols with oleic acid and methacrylic acid. • Esterification of resulted copolymers with two moles of fatty alcohol	• Evaluated on crude oil from Gandhar oil field (Gujarat, India). • Depress the pour point of the crude oil up to 9ºC with 500 ppm of doses.
Hafiz *et al.*, 2007	• Preparation of olefin maleic anhydride copolymers by reacting C_8 or C_{14} olefin with maleic anhydride, then esterified with dodecyl alcohol	• 12ºC & 18ºC reduction at 1000ppm of crude oil pour point of 24ºC & 15ºC
Deshmukh *et al.,* 2007	• Synthesis of Poly (n-alkyl acrylates-co-N-hexadecylmaleimide) by the reaction of copolymers with hexadecylamine.	• Evaluated on Nada crude oil (Gujarat, India) • 27ºC reduction at 1000 ppm & 21ºC at 500 ppm of crude pour point of 30ºC
Taraneh *et al.,* 2008	• Synthesis of ethylene-vinyl acetate copolymer (EVA) with different ranges of molecular weight	• Evaluated on Iranian waxy crude oils with pour point of 8ºC to 26ºC
Wu *et al.,* 2012	• Designed and synthesized maleic anhydride co-polymer and its derivatives with different polar and/or aromatic pendant chains	• Evaluated on Changqing (CQ) crude • Depress the pour point by 19 °C and decrease the yield stress as well as viscosity to a large extent.

CHAPTER 3

METHODOLOGY

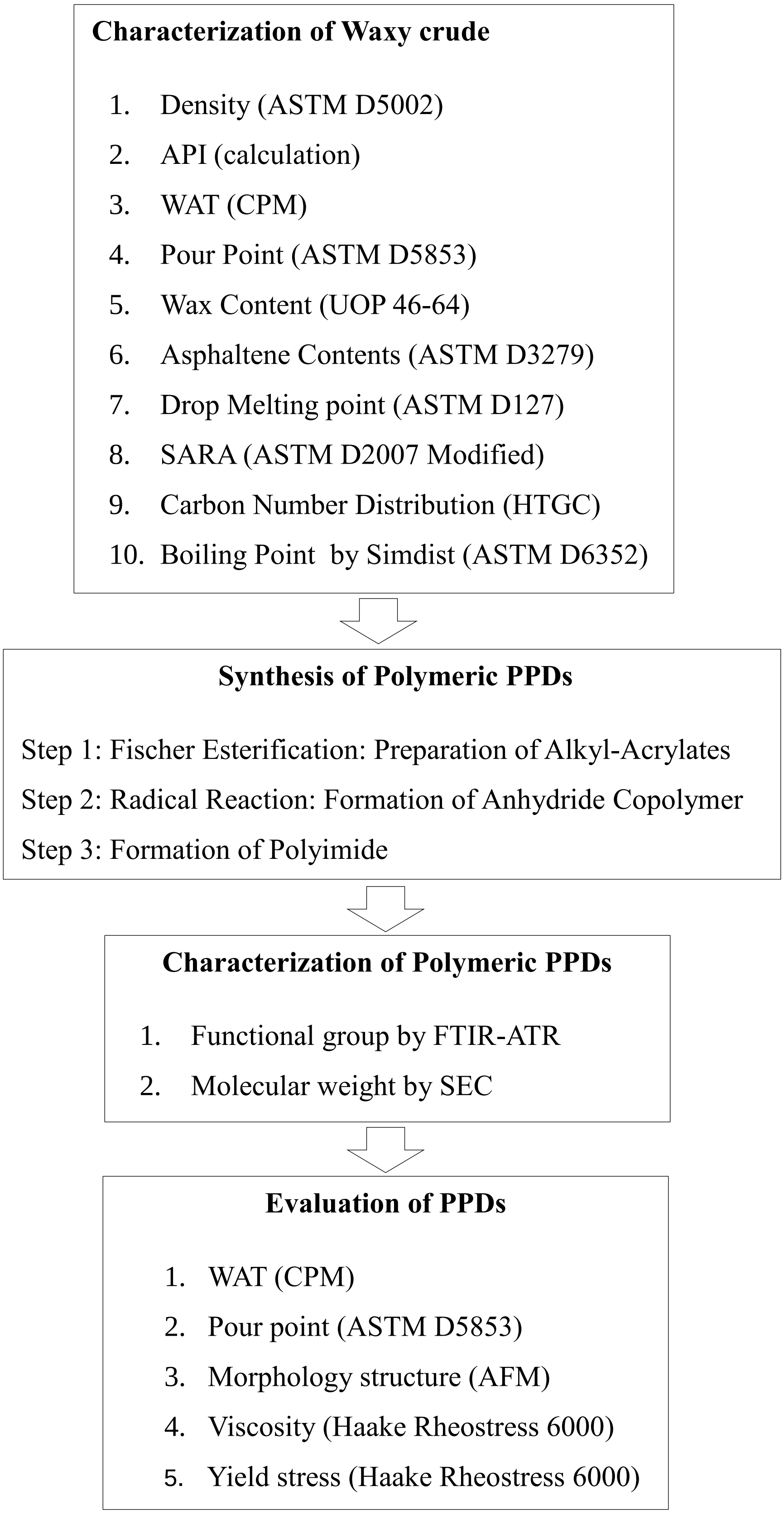
The objectives of the research were achieved by following certain protocols. Two Malaysian waxy crudes were investigated for their density, API gravity, WAT, pour point, wax content, asphaltene content and carbon distribution.

The PPDs were then synthesized in three steps involving preparation of acrylates of five different alkyls and then copolymerizing them with maleic anhydride to produce five anhydride copolymers. The anhydride copolymers were subsequently reacted with hexadecylamine to produce Poly (n-alkyl acrylates-co-N-hexadecylmaleimide). The synthesized PPDs were characterized by FTIR-ATR and SEC to confirm the presence of their functional groups and to determine their molecular weight, respectively.

The synthesized and commercial PPDs were evaluated for their performance as flow improvers on two Malaysian waxy crude oils having high WAT and pour point in terms of the pour point depression, WAT, viscosity and yield stress reduction. The crystal morphology changes in the treated waxy crudes were also studied by AFM.

This chapter has been organized into various sections to elucidate the experimental procedures, theoretical background and working principle of the utilized equipment. Section 3.1 is related to the crude characterization. Section 3.2 and Section 3.3 describe the synthesis and characterization of PPDs, respectively. Section 3.4 elaborates on the evaluation of PPDs.

The workflow of the research methodology is summarized in Figure 3.1.



Characterization of Waxy crude

1. Density (ASTM D5002)
2. API (calculation)
3. WAT (CPM)
4. Pour Point (ASTM D5853)
5. Wax Content (UOP 46-64)
6. Asphaltene Contents (ASTM D3279)
7. Drop Melting point (ASTM D127)
8. SARA (ASTM D2007 Modified)
9. Carbon Number Distribution (HTGC)
10. Boiling Point by Simdist (ASTM D6352)

Synthesis of Polymeric PPDs

Step 1: Fischer Esterification: Preparation of Alkyl-Acrylates
Step 2: Radical Reaction: Formation of Anhydride Copolymer
Step 3: Formation of Polyimide

Characterization of Polymeric PPDs

1. Functional group by FTIR-ATR
2. Molecular weight by SEC

Evaluation of PPDs

1. WAT (CPM)
2. Pour point (ASTM D5853)
3. Morphology structure (AFM)
4. Viscosity (Haake Rheostress 6000)
5. Yield stress (Haake Rheostress 6000)

Figure 3.1: Workflow of research methodology

3.1 Crude Oil Characterization

Highly waxy crudes were characterized by means of physicochemical analysis (WAT, pour point and API gravity) and hydrocarbon analysis (wax content, asphaltene content and carbon number distribution). The tests were conducted by ASTM standard test procedures and by equipment manuals.

3.1.1 Density Measurements

The crude density was determined by ASTM D5002 method using a DMA 48 Density Meter with a measuring range of 0 to 3 g/cm^3, repeatability of ±3 x 10^{-5} g/cm^3, a temperature accuracy of 0.01 ºC and a temperature range of -10 ºC to 70 ºC.

The instrument was calibrated when first setting up and whenever the test temperature was changed. Thereafter, the calibration checks were conducted at least weekly during routine operation or more frequently as may be dictated by the nature of the crude oils being measured. Distilled water was used for the instrument calibration.

About 0.7 mL of crude oil was introduced into the clean, dry, sample tube of the instrument using a suitable syringe (Figure 3.2a). The syringe was left in place and the exit port was plugged. Then the illumination light was turned on and the sample plug tube was examined carefully to make sure that there was no obvious presence of bubbles trapped in the U-tube, and that it was filled completely. The sample must appear to be homogeneous. The illumination light was turned off immediately after inspection of the sample tube, since the heat generated affects the measurement temperature.

The sample was allowed to equilibrate to the test temperature before proceeding to evaluate the test sample for the presence of unseen air or gas bubbles. For dark crude oil samples the observation of air or gas bubbles in the sample tube was very difficult. The presence of bubbles can often be detected, however, by observing the fluctuations of the digital display of density value. Air or gas bubbles cause large random variations in the third and fourth significant figures for density reading. When bubbles were absent and the sample was at equilibrium with the test temperature, the displayed values were stable and showed only small variations of the order of 1 to 2 units in the last significant figure. If stable values were not observed after a few minutes, the test was repeated by injecting a new sample into the tube.

After the instrument displayed a steady reading to four significant figures for density indicating that temperature equilibrium has been reached, the density reading was recorded as shown in Figure 3.2b.

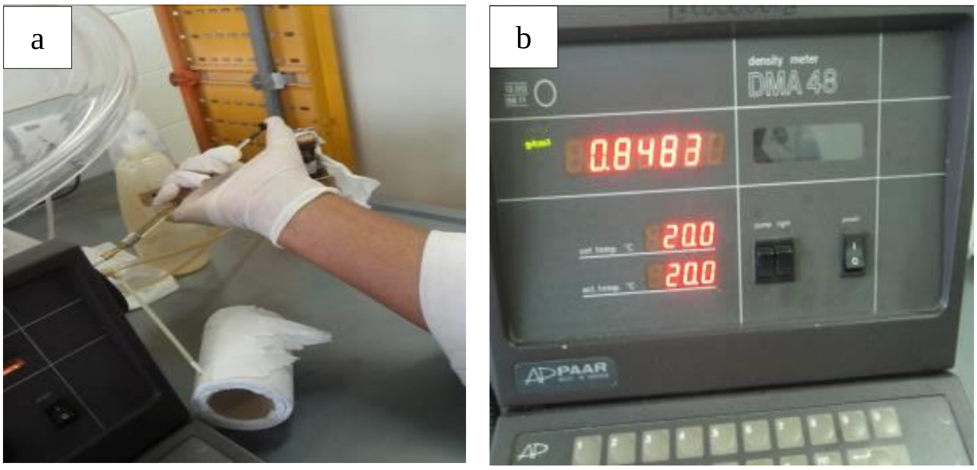


Figure 3.2: DMA 48 a) Injecting sample through a sample port, b) Density readout

3.1.2 API Gravity

API gravity is a measure of the gravity (weight per unit volume) of crude oil or other related liquids as measured by a system recommended by the American Petroleum Institute. API Gravity is expressed in degrees, a specific gravity of 1.00 being equivalent to 10°API. API gravity is related to specific gravity (SG) by the following relation presented in formula (1) and (2).

$$SG\ oil = \rho oil/\rho water \tag{1}$$

$$API\ Gravity = \left(\frac{141.5}{SG}\right) - 131.5 \tag{2}$$

3.1.3 Wax Appearance Temperature (WAT)

WAT of black oil is usually inferred from viscometry, differential scanning calorimetry (DSC) or Cross Polar Microscopy (CPM). CPM is generally deemed to be the most sensitive and the only direct visual technique applicable for all non-biodegraded oils including opaque fluids (Hammami *et al.*, 1999; Erickson *et al.,* 1993). This technique is considered the most accurate technique for the determination of WAT since it can identify the very first crystal of wax.

CPM measures the temperature at which wax crystals can be seen via microscopy under cross polarized light. The basis for the determination relies on the fact that light was prevented from passing through two polarizing filters that were set 90° apart. The oil sample was placed between the cross-polarized filters, and any crystalline material present will rotate the light allowing the light to pass through the second polarization filter. Therefore, during the experiment what was observed was a dark sample in which spots (or other shapes depending on magnification) were seen as the temperature was lowered.

In this analysis, the sample was preheated at 90°C for 30 minutes and a thin layer of the sample was transferred to a microscopy slide (Figure 3.3a), which was connected to a controlled refrigeration system (Figure 3.3b). The sample was cooled in increments of 1°C, until crystalline material can be seen. The first white dot was seen as the first wax crystal appeared upon reaching WAT (Lee *et al.*, 2007). Then the sample was cooled to at least 1°C beyond the point where crystalline material was first seen and it was observed that additional crystalline material was precipitating from solution (Figure 3.3c).

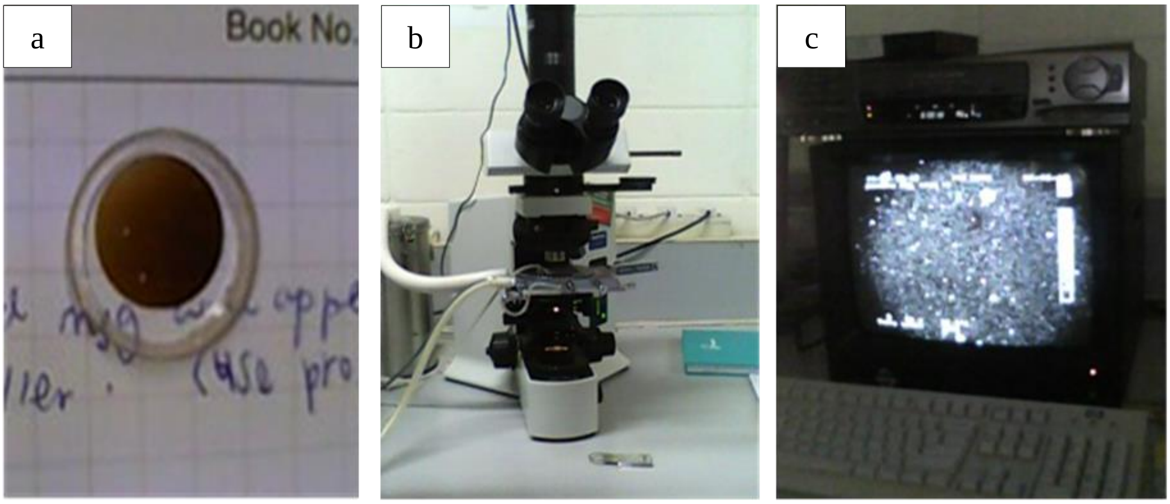


Figure 3.3: CPM a) Sample microscopy slide, b) Microscope, c) Image on screen

3.1.4 Pour Point

A procedure for testing the pour point of crude oils is described in ASTM D5853, where it covers the determination of both maximum and minimum pour point temperatures. The maximum pour point is obtained after the sample has been subjected to a prescribed treatment designed to enhance gelation of wax crystals and solidification of the sample; and the minimum pour point is obtained after the sample has been subjected to a prescribed treatment designed to delay gelation of wax crystals and solidification of the sample.

In this study, only maximum pour point was performed as the following procedure. The crude oil was heated in a test jar to a temperature of at least 20°C above its expected pour point. The jar was fitted with a thermometer with its bulb immersed to a depth that places the beginning of the capillary 3 mm below the surface of the sample. The whole arrangement was then allowed to cool to room temperature for at least 24 hours. The pour point of crude is dependent on the state of crystallization of the wax in the test specimen; and achieving equilibrium between crystallized wax and dissolved wax in crude oil is reached within 24 hours (ASTM D5853).

After 24 hours, the sample in a test jar was heated to 80°C and gently stirred with a spatula as soon as it reached 80°C. The sample was cooled down by putting it into a water bath with a temperature maintained at 0°C (Figure 3.4a). The appearance of the sample was examined when the sample temperature was at 60°C (estimated as a multiple of 3°C).

The tube containing the sample was tilted at 45° to observe any fluid movement as shown in Figure 3.4b. The test jar was immediately returned to the water bath if there was any fluid movement observed. This step was repeated for every 3°C temperature drop until the sample ceased to move when tilted at 45° angle.

Once the sample ceased to move when tilted, the jar was held horizontally for 5 seconds to observe any fluid movement (Figure 3.4c). The test jar was immediately returned to the water bath if fluid movement was observed before 5 seconds has passed. This step was repeated until a point was reached at which the sample showed no movement when the jar was held in a horizontal position for 5 seconds. The observed reading was recorded and reported as the pour point of the sample by adding 3°C.

A new crude sample was heated to 20°C above its expected pour point before treating it with synthesized PPDs. The pour point measurement for sample treated with PPD was conducted following the steps in pour point determination for virgin crude.

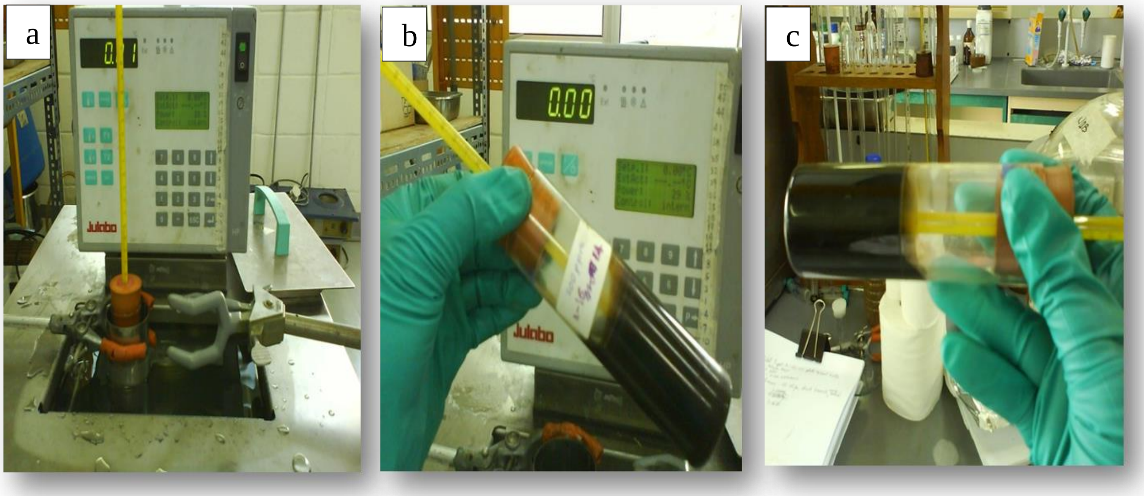


Figure 3.4: a) Pour point water bath, b) Jar tilted at 45° c) Jar in horizontal position

3.1.5 Wax Content

The wax content for the samples was determined using UOP 46-64 method. About 2 g of a given sample was dissolved in petroleum spirit (40/60). The solution was clarified using bole white and filtered through 47 mm filter paper. The residue was dissolved with hot petroleum spirit, which was then evaporated using rotary evaporator. The resulted residue was dissolved in an acetone-petroleum spirit (75:25) mixture. This solution was then chilled in a water-glycol bath (50:50) at -17ºC for an hour. Then it was filtered through a cold filter funnel and the wax was collected on a 47 mm filter paper in the funnel.

The wax was subsequently washed from the filter paper into a weighed flask with hot petroleum spirit. Finally, the petroleum spirit was evaporated and the precipitated wax was dried in an oven at 105ºC, cooled in a dessicator and weighed until constant weight. The step by step procedure is in Appendix II.

3.1.6 Drop Melting Point

The drop melting point was determined by ASTM D127 in which the samples were deposited on two thermometer bulbs by dipping chilled thermometers into the sample. The thermometers bearing the samples were placed in test tubes and heated by means of a water bath until the samples melted and the first drop fell from each thermometer bulb. The average of the temperatures at which these drops fall was the drop melting point of the sample.

3.1.7 Asphaltene Content

ASTM D3279 covers the determination of the mass percent of asphaltenes as defined by insolubility in n-heptane. About 1.0 g of crude sample and 100 mL of n-heptane (Analar grade) was added into a 250 mL Erlenmeyer flask. The solution was refluxed gently for about 30 minutes and cooled to room temperature for 1 hour before filtering it through a glass-fiber pad. The insoluble material was washed with three portion of n-heptane of about 10 mL each. Then it was dried in the 107ºC oven for 15 minutes, cooled in dessicator and weighed to the nearest 0.1 mg.

The mass percent of n-heptane insoluble (NHI) was calculated as the percentage of the original sample as in equation (3).

$$n - heptane\ insolubles, wt\% = (A/B) \times 100 \tag{3}$$

Where:
A = total mass of insolubles
B = total mass of sample

3.1.8 Saturates, Aromatics, Resins and Asphaltenes Content (SARA)

Detailed crude oil composition could not be properly determined due to the high number of compounds present in the mixture. It is commonly accepted to group the different compound present in crude oils in different families according to their chemical structure, PNA (paraffin, naphthenes, aromatic) or polarity, SARA (saturates, aromatics, resins and asphaltenes) (Altgelt and Boduszynki, 1994).

SARA test was conducted using ASTM D2007 modified method where it enables the isolation of volatiles, saturates (S), aromatics (A), resins (R) and asphaltenes (A). The separation process was based on differences in solubility and polarity. The test involved several steps as shown in Appendix III.

Step 1: Determination of Loss on Heating at 100^{o}C

0.50 g sample was dried for 5 hours in an oven at 100ºC, cooled in a dessicator for 10 minutes and weighed. The sample was dried and cooled repeatedly until a constant weight was obtained. The volatile, wt % was calculated by equation below.

$$Volatiles, wt\ \% = \left(\frac{A-B}{A}\right) \times 100 \tag{4}$$

Where:
A = wt of original sample
B = wt of dry sample

Step 2: Determination of n-pentane Insoluble

The dried sample from Step 1 was transferred to a round-bottom flask where 200 mL of n-pentane (Analar grade) was added. The mixture was refluxed for 1 hour and kept overnight in the dark. The residue was filtered through a pre-weighed Whatman No.1 filter paper and rinsed with 30 mL n-pentane.

The filtrate was kept for determination of saturates, aromatics and resins. The weight of n-pentane insoluble was obtained by drying and weighing the filter paper to a constant weight. The residue or n-pentane insoluble is assumed to contain all the asphaltene present in the solution.

$$n - pentane\ insolubles,\ wt\% = (A/B) \times 100 \tag{5}$$

Where:
A = wt of residue
B = wt of sample

Step 3: Determination of Saturates Content

Forty gram of silica gel (Grade 923, pore size 30A, 100-200 mesh from Sigma-Aldrich) was weighed, heated in an oven at 100ºC for 3 hours and cooled in a dessicator and packed into a column. Small portion of n-pentane (Analar grade) was poured into the silica gel packed column to avoid air trapped as shown in Figure 3.5.

Figure 3.5: Silica gel packed column

The filtrate from Step 2 was poured into the column and allowed to elute until very small portion was left above the column. The filtration flask was rinsed with 3-4 small portions of n-pentane and the washings were poured into the column. The column was further eluted with n-pentane until 300 mL of eluted solution was collected in a 500 mL round-bottom flask. The excess n-pentane was distilled off and the content of the round bottom flask was dried in an oven to a constant weight. Saturates, wt % was calculated by equation (6).

$$Saturates, wt\% = (A/B) \times 100 \quad (6)$$

Where:

A = wt of residue

B = wt of sample

Step 4: Determination of Aromatics Content.

The column was eluted with small portions of toluene until 300 mL of eluted solution was collected in 500 mL round bottom flask. The excess toluene was distilled off and the content of the round bottom flask was dried in an oven to constant weight. Aromatic, wt % was calculated by the following equation.

$$Aromatics, wt\% = (A/B) \times 100 \tag{7}$$

Where:
A = wt of residue
B = wt of sample

Step 5: Determination of Resin Content

The column was eluted with 200 mL mixture of 10% methanol: 90% toluene into a 500 mL round-bottom flask. The excess solvent was distilled off and the content of the round bottom flask was dried in an oven until constant weight was obtained. The Resin, wt% was calculated by the equation below.

$$Resin, wt\% = (A/B) \times 100 \tag{8}$$

Where:
A = wt of residue
B = wt of sample

3.1.9 Carbon Number Distribution

The compositional characterization of waxes was conducted according to ASTM D7169 by High Temperature Gas Chromatography (HTGC) for the identification of waxes up to 100 carbon atoms. During HTGC, compounds of high boiling point were kept mobile as the column was heated to and stabilized at 500°C.

In general, chromatography is a term that describes techniques used to separate components of mixtures. In HTGC, the gaseous mobile phase is forced through the stationary phase using pressure. The equipment consists of a gas tank, pressure and flow regulators to control the gas flow, an oven, an injector to allow injection of a small volume of the sample mixture under pressure, a column containing the bed of stationary phase, a detector to detect the presence of components as they exit the column, and some means to record the detector signal.

The column used for HTGC analysis is a steel clad capillary column DB-5HT 30 m length, 0.32 mm internal diameter (ID), 0.10 μm film thickness (by Agilent).

The sample was diluted into 2 wt % and injected into chilled column. The operating conditions for the HTGC analysis are tabulated in Table 3.1. The chromatographic spectrum was then compared with the standard for component identification. The wt% of carbon distribution was calculated from area count of each component.

Table 3.1: Operating conditions for the HTGC analysis

Carrier gas	
Name	Helium
Pressure (psi)	44
Column	
Type	DB-5HT
Initial temperature (°C)	30
Final temperature (°C)	325
Programming rate (°C/min)	10
Detector	
Type	FID
Temperature (°C)	350
Gases, Hydrogen (ml/min)	40
Air (ml/min)	450
Injector	
Type	Split
Initial temperature (°C)	350
Sample	
Size (μL)	1

3.1.10 Cold Finger

Both untreated crude and crude treated with PPD-A16 were subjected to cold finger procedure for waxes extraction. The extracted waxes were then evaluated for the effectiveness of the PPD-A16 to reduce the boiling point of the waxes.

Procedure

1. I L of sample was heated to 90ºC for at least 1 hour.
2. The sample was poured into the coaxial glass with magnetic bar.
3. The coaxial glass was put in the heater system set at 90ºC
4. The sample was stirred at 200 rpm for at least 30 minutes.
5. The cold finger probe was inserted into the sample with the cooling temperature set at 20ºC
6. The wax deposited on the cold finger probe was collected after 15 minutes.

3.1.11 Simulated Distillation (ASTM D6352 Modified)

This is a gas chromatographic method utilizing an inlet and a capillary column, both of which are subject to a temperature program. A flame ionization detector is used as a transducer that converts mass to an electrical signal. A data acquisition system operating in the slice mode and chromatography software is used to accumulate the electronic signal. A retention time calibration mixture is used to develop a retention time versus boiling point curve.

The boiling range distribution determination by distillation was simulated by the use of gas chromatography. A sample aliquot was diluted with a viscosity reducing solvent and introduced into the chromatographic system. The normalized cumulative corrected sample areas for each consecutive recorded time interval were used to calculate the boiling range distribution. The boiling point temperature at each reported percent off increment was calculated from the retention time calibration.

The column used for Simdist analysis is a steel clad packed column Cp simdist ultimetal 5m length, 0.53 mm internal diameter (ID), 0.17 μm film thickness (by

Perkin Elmer). The operating conditions for the Simdist analysis by gas chromatographic are tabulated in Table 3.2.

Table 3.2: Operating conditions for the Simdist analysis by gas chromatography

Carrier gas	
Name	Helium
Flowrate (ml/min)	12
Column	
Type	Cp simdist ultimetal 5m
Initial temperature (°C)	-10
Final temperature (°C)	435
Detector	
Type	FID
Temperature (°C)	435
Gases, Hydrogen (ml/min)	40
Air (ml/min)	450
Injector	
Type	PTV
Initial temperature (°C)	30
Final temperature (°C)	435
Sample	
Size (µL)	1
Concentration mass (%)	10

3.2 Synthesis of Polymeric PPDs

In the industry, there is no known "universal" flow enhancer; however, a great number of wax-treating chemicals are derivatives of maleic anhydride (Son *et al.,* 1993). As such this study was focused on this widely used chemistry where the performance of various esters of copolymers of maleic anhydride was compared using laboratory tests designed to simulate offshore conditions (shear rates and temperatures).

In this study, the synthesis of the polymeric PPDs was based on the published work of Deshmukh and Bharambe, 2007. The calculations and step by step procedures are depicted in Appendix IV.

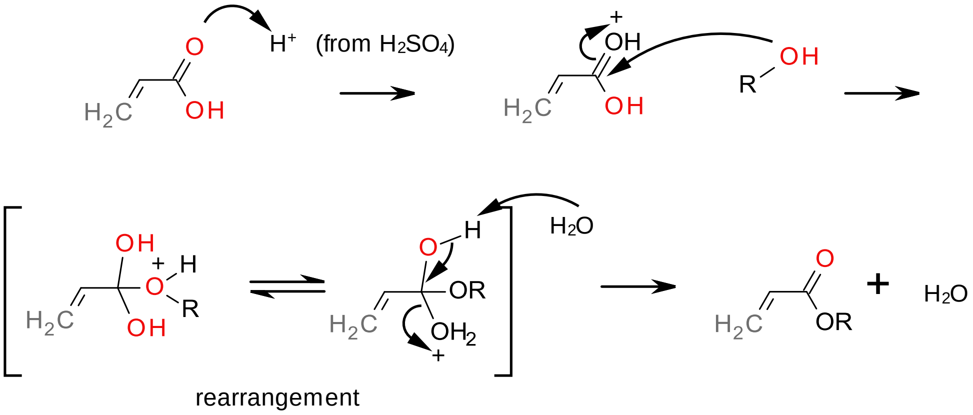
Materials

1. Acrylic acid, 99.5% (Merck Chemicals)
2. n-alkyl alcohol (n = 10, 12, 14, 16, 18)
    a) 1-Decanol, 99% (Sigma-Aldrich; $C_{10}H_{22}O$; Mw=158.28 g/mol; ρ=0.829)
    b) 1-Dodecanol, 98% (Sigma-Aldrich; $C_{12}H_{26}O$; Mw=186.34 g/mol; ρ=0.820)
    c) 1-Tetradecanol, 97% (Sigma-Aldrich; $C_{14}H_{30}O$; Mw=214.39 g/mol)
    d) 1-Hexadecanol, 99% (Sigma-Aldrich; $C_{16}H_{34}O$; Mw=242.44 g/mol)
    e) 1-Octadecanol, 95% (Acros-Organic; $C_{18}H_{38}O$; Mw=270.50 g/mol)
3. Sulfuric acid, 99% (Sigma-Aldrich)
4. Maleic anhydride, 99% (Acros-Organic)
5. Benzene, AnalaR Grade, 99.7% (BDH)
6. Benzoyl peroxide, 75% (Acros-Organic)
7. Methanol, AnalaR Grade, 99.8% (BDH)
8. 1-Hexadecylamine, 90% (Acros-Organic)
9. Toluene, AnalaR Grade, 99.5% (BDH)
10. Nitrogen, 99.9% (MOX)

Procedure

Three reaction steps in the synthesis of polymeric PPDs include firstly the Fisher esterification, followed by the radical reaction in the formation of anhydride copolymer and finally the formation of polyimide.

Step 1: Fischer Esterification



Scheme 1

1 mol of acrylic acid was reacted with 1 mol of five different n-alkyl alcohols (n= 10, 12, 14, 16, 18) using sulfuric acid as catalyst. Water was separated azeotropically using Dean-Stark apparatus. The reaction steps are as shown in Scheme 1.

The molarity for n-alkyl alcohol (in liquid form) was calculated by the following relationship (1-Decanol, n10: Purity = 99%; Mw= 158.28 g/mol; Density: 0.829).

$$Molarity = \left(\frac{Density}{Molecular\ weight} \times \frac{\%\,purity}{100}\right) \times 1000 \qquad (9)$$

$$= \left(\frac{0.829}{158.28} \times \frac{99}{100}\right) \times 1000$$

$$= \ 5.185\ \text{M}$$

Using the relationship of $M_1V_1 = M_2V_2$ (10)

$$V_1 = \frac{M_2V_2}{M_1}$$

Where;

M_1 = the molarity of 1-Decanol (n10)

V_1 = the required volume of 5.185 M 1-Decanol to prepare 1M 1-Decanol in 250 ml

$$V_1 = \frac{1\ \times 250}{5.185}$$

= **48.21 mL 1-Decanol**

The same calculation was used for Acrylic acid which was in liquid form.
Purity = 99.5%; Mw= 72.06 g/mol; Density= 1.050 g/L

$$Molarity\ of\ acrylic\ acid = \left(\frac{1.05}{72.06} \times \frac{99.5}{100}\right) \times 1000$$
$$= \ 14.498\text{ M}$$

The required volume of 14.498 M Acrylic acid to prepare 1M Acrylic acid in 250 mL;

$$V_1 = \frac{1\ \times 250}{14.498}$$

= 17.24 mL Acrylic acid

Thus, 48.21 mL of 1-Decanol (n10) was reacted with 17.24 mL of Acrylic acid in 250 mL solution with a few drops of concentrated sulfuric acid added as catalyst.

The calculation for solid alkyl alcohols was different from the calculation of liquid alcohols above.

1-Hexadecanol (n16) with Mw= 242.44 g/mol in 1 L solution.

$$\frac{242.44\ g}{1000\ mL} = \frac{wt}{75\ mL}$$

$$wt = \frac{242.44\ g}{1000\ mL} \times 75\ mL$$

= 18.183 g of 1-Hexadecanol

Volume of Acrylic acid required;

$$V_1 = \frac{1\ \times 75}{14.4983}$$

= 5.17 mL of Acrylic acid

Therefore, 18.183 g of 1-Hexadecanol and 5.17 mL of acrylic acid were mixed in the round bottom flask. The solution was then made up to 75 mL with distilled water; and few drops of concentrated sulfuric acid were added as catalyst.

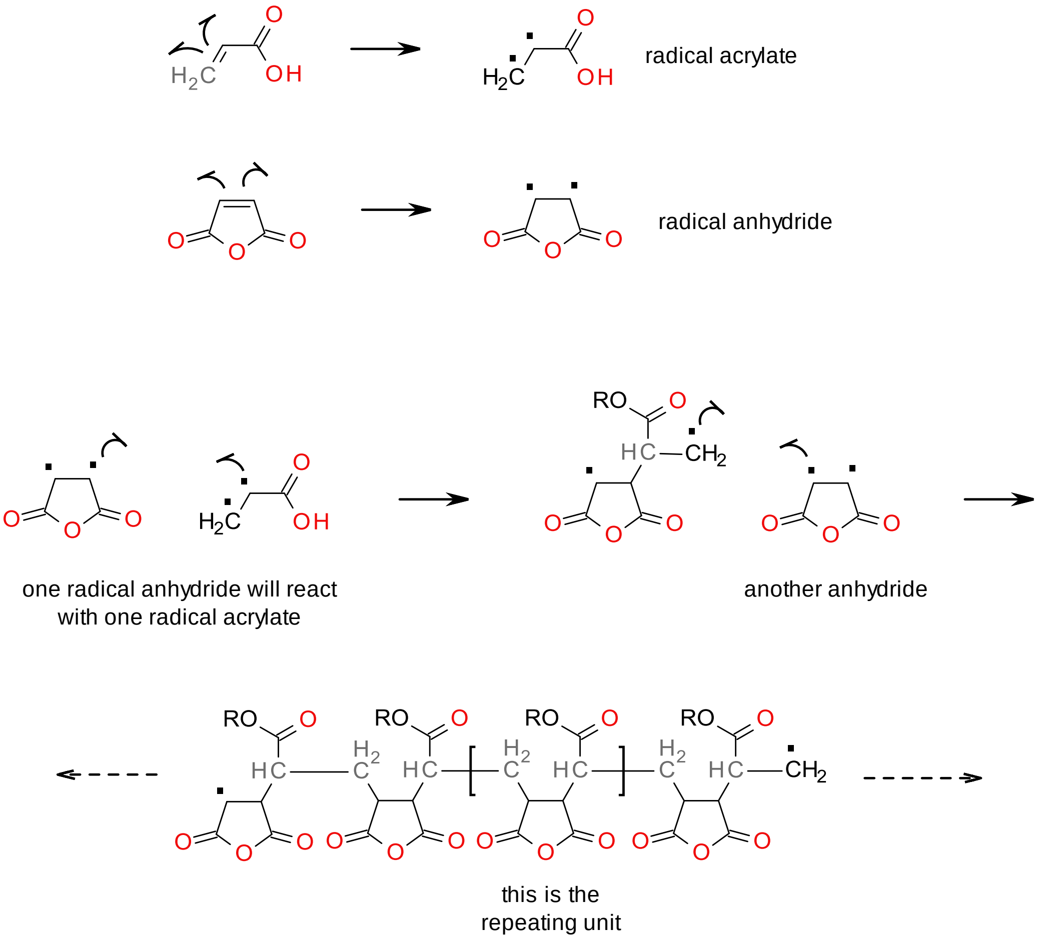
The calculated amounts of alcohols and acetic acid required in the synthesis are summarized in Table 3.3.

Table 3.3: Required chemicals in Fischer Esterification

n-Alkyl acrylates	Alcohol	Acrylic Acid, mL	Total volume of solution, mL
n10	48.21 mL	17.24	250
n12	57.97 mL	17.24	250
n14	16.08 g	5.17	75
n16	18.18 g	5.17	75
n18	20.29 g	5.17	75

The density of the obtained alkyl acrylates was determined by ASTM D5002 using a DMA 48 Densitometer as shown in Appendix V.

Step 2: Radical Reaction- Formation of Anhydride Copolymer



Scheme 2

a) In a 100 mL three-neck round flask fitted with a condenser, a temperature controller and a nitrogen-controlled inlet valve, the n-alkyl acrylates and maleic anhydride were added in 1:1 mole ratio in dry benzene under nitrogen atmosphere using benzoyl peroxide as initiator (1% by wt) at 60-70˚C with constant stirring for 7-8 hours (Figure 3.6a).

b) After the reaction has completed (Scheme 2), benzene was distilled off under reduce pressure by keeping it at 60˚C under vacuum for 2-3 hours (Figure 3.6b).

c) The copolymers were purified by precipitation in excess volume of methanol and then vacuum dried for 24 hours.

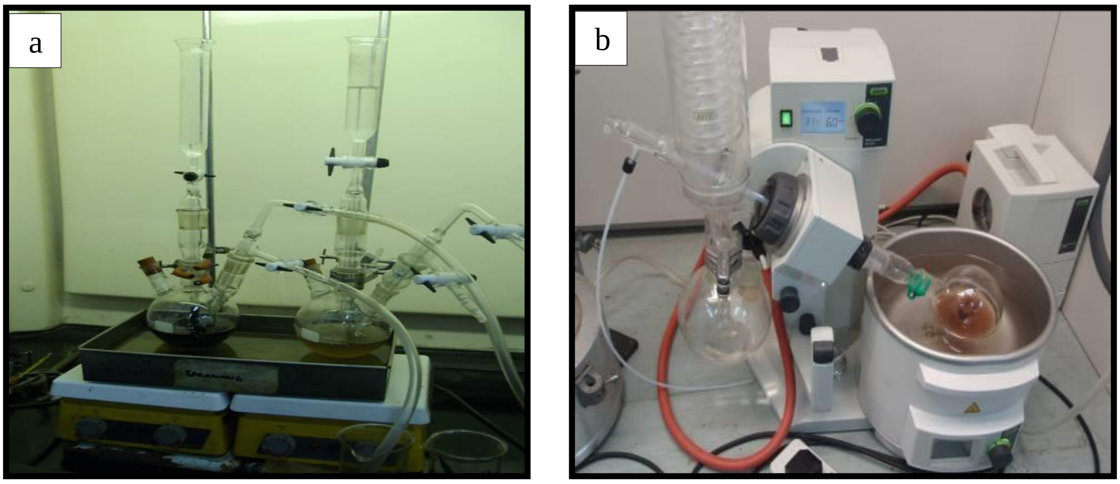


Figure 3.6: Synthesis of PPDs a) Refluxing assembly b) Rotary evaporator

46 mL of n-decyl acrylate, n10 (Mw= 191 g/mol) obtained from step 1

$$Density = \frac{Mass}{Volume} \qquad (11)$$

$$mass \ = 0.8364 \frac{g}{mL} \times 46\, mL$$

= 38.47 g

Mass of n-decyl acrylate = 38.47 g

$$Mw = \frac{mass}{mol} \qquad (12)$$

$$mol = \frac{38.47\ g}{191\ g/mol}$$

Mol of n-decyl acrylate, n10 =0.2014 mol

Mw of Maleic Anhydride = 98.06 g/mol

$$Mass = mol\ \times Mw$$

$$= 0.20\, mol\ \times 98.06\ g/mol$$

Mass of Maleic Anhydride = 19.75 g

Benzoyl Peroxide used was 1% from the total weight of n-acrylate and Maleic Anhydride (Total weight = 38.47 g + 19.75 g = 58.22 g).

Mass of Benzoyl peroxide = 1% of 58.22g = **0.58 g**

The calculated amounts of chemicals required in the preparation of anhydride copolymers are summarized in Table 3.4.

Table 3.4: Required chemicals in preparation of anhydride copolymers

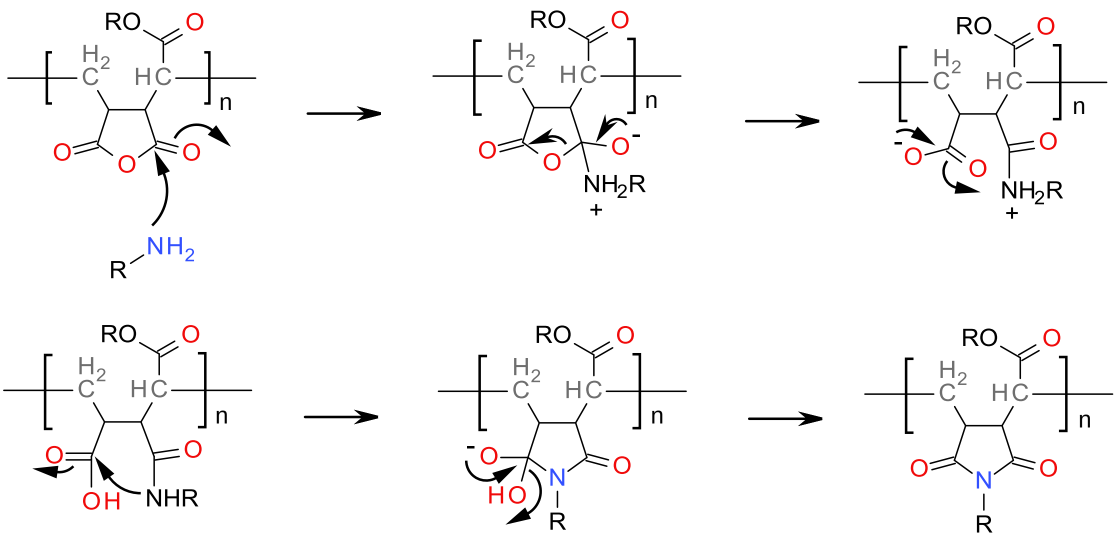
n-Alkyl acrylate	Mw of n-Alkyl acrylate	Density of n-Alkyl acrylate	Volume of n-Alkyl acrylate, g	Mass of n-Alkyl acrylate, g	Amount of Maleic Anhydride, g	Amount of Benzoyl peroxide g	Total volume of Benzene, mL
n10	191	0.8364	46	38.47	19.75	0.58	200
n12	215	0.8481	53	44.95	20.50	0.65	200
n14	239	NA*	NA*	28.61	11.74	0.40	200
n16	263	NA*	NA*	63.81	23.79	0.88	200
n18	287	NA*	NA*	26.73	9.13	0.36	200

Note:

NA*= not applicable since n14, n16 and n18 acrylates were in solid form.

Step 3: Formation of Polyimide

The resultant copolymers from Step 2 were allowed to react with hexadecylamine in 1:1 molar ratio in presence of molecular sieves using toluene as a solvent for 10-15 hours (Appendix II).



Scheme 3

Wt of Anhydride copolymer (n10) = 28.7g

Mw of anhydride copolymer (n10) = 226 g/mol.

Using the relationship in equation (12);

$$mol = \frac{28.7}{226} = 0.127$$

Mw of hexadecylamine = 241.46 g/mol

$$\boldsymbol{wt\ of\ hexadecylamine} = 0.127\ mol\ \times 241.46\ {}^{g}/_{mol} = \mathbf{30.67\ g}$$

It was determined that only 2 ml of toluene was needed to dissolve 0.4 g of hexadecylamine. Hence, the amount of toluene needed to dissolve 30.67 g hexadecylamine;

$$\frac{0.4g\ hexadecylamine}{2\ mL\ toluene} = \frac{30.67g\ hexadcylamine}{x\ mL\ toluene}$$

$$x\ mL\ toluene = \frac{30.67\ \times 2}{0.4}$$

= 153.35 mL Toluene

The same calculations were used for anhydride copolymer of n12, n14, n16 and n18.

The calculated amounts of chemicals required in the preparation of polyimide are summarized in Table 3.5.

Table 3.5: Required chemicals in the preparation of polyimide

n-alkyl acrylate	Mw of n-alkyl acrylates, g/mol	Mass of anhydride copolymers, g	Mw of hexadecylamine, g/mol	Mass of hexadecylamine, g	Volume of Toluene, mL
n10	226	28.70	241.46	30.67	153.35
n12	250	20.08	241.46	19.39	96.95
n14	274	21.19	241.46	18.67	93.35
n16	298	29.14	241.46	23.61	118.05
n18	322	18.64	241.46	13.98	69.90

3.3 Characterization of PPDs

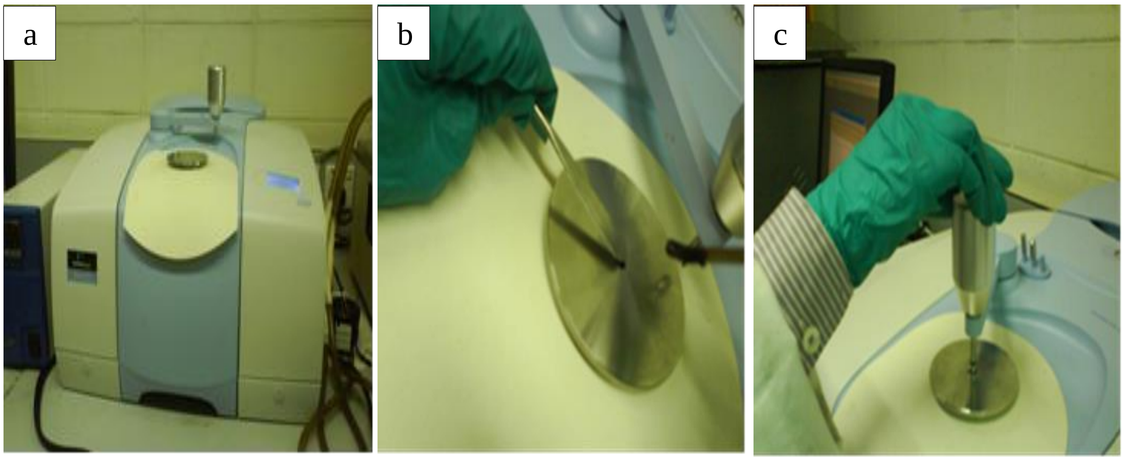
Synthesized PPDs were characterized using FTIR-ATR and SEC to confirm the presence of the functional groups and to determine the molecular weight of the PPDs, respectively.

3.3.1 FTIR-ATR Spectroscopy

The main objective of Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR) spectroscopic analyses is to determine the chemical functional groups present in the sample. Different functional groups are susceptible to absorb characteristic frequencies of IR radiation. FTIR-ATR spectroscopy is an important and popular tool for structural elucidation and the identification of various compounds. Specific IR reflectance techniques may be divided into the areas of specular reflectance, diffuse reflectance, and internal reflectance. The latter is often termed as attenuated total reflectance (Ferraro *et al.*, 1990).

FTIR-ATR spectra of the samples were recorded using the Perkin Elmer-Spectrum 400 FTIR-ATR spectrometer (Figure 3.7a) by placing a droplet of the sample in-between diamond-composite FTIR-ATR sample holding plate (Figure 3.7b). The sample holding plates were equipped with a load to spread the sample uniformly and tightly against the diamond surface (Figure 3.7c). FTIR-ATR spectra were obtained by averaging 10 scans from 350 cm^{-1} to 6000 cm^{-1} wavelength at a resolution of 2 cm^{-1}. A spectrum from the diamond-composite plates was recorded as a background; and the spectrum results appeared on the computer's screen after a few minutes.

The step by step procedure is shown in Appendix VI.



The bands of carbonyl group, symmetric, asymmetric, and rocking vibrations of CH groups, symmetric and asymmetric modes of carboxylate ions are appeared as described in Table 3.6 (Didukh *et al.*, 2004). Peak at 1095 cm^{-1} is responsible for C-O-C groups. The intensive peak at 1712 cm^{-1} belongs to stretching vibrations of C=O groups. Asymmetric vibration of carboxylic groups is appeared at 1570 cm^{-1}.

Table 3.6: Reported wavelength (Didukh et al., 2004)

Figure 3.7: a) FTIR-ATR b) Sample holding plate c) Sampler spreader

Functional groups	**Frequency,^{a} cm^{-1}**
$v(CH)_{as}$	2923 (vs)
$v(CH)_{s}$	2853 (s)
$v(C=O)$	1712 (vs)
$v(COO^{-})_{as}$	1570 (s)
$v(COC)_{as}$	1095 (w)

(Band intensities and vibration types: vs-very strong; s-strong; w-weak; s-symmetric; as-asymmetric)

3.3.2 Molecular Weight Characterization by SEC

Due to the statistical nature of polymerizations, synthetic polymers possess a combination of molecules having a range of different molecular weights creating a wide distribution of molecular chain lengths. The complete extent of the molecular weight distribution, which determines the physical properties of the polymer, mainly depends on the polymerization process. It is then important to derive an average molecular weight which can be used to characterize each individual polymer.

Size Exclusion Chromatography (SEC) is the most widely used method of molecular weight determination. The principle operational method of SEC is the separation of polymer molecules based on their hydrodynamic size (radius) or volume, not molecular weight. In order to calculate molecular weight parameters, SEC systems are operated under Triple/Tetra detection mode.

Triple/Tetra detection consists of a concentration detector (Refractive index detector), an online dilute solution viscometer and a molecular weight sensitive (Static light scattering) detector. The Viscometer determines intrinsic viscosity and hydrodynamic radius and the Light scattering detector measures absolute molecular weight.

The weight average molecular weight (Mw) of PPD-A16 was analyzed using the Viscotek TDAmax Triple Detection SEC system by Malvern as shown in Figure 3.8. The analysis parameters are tabulated in Table 3.7.

Figure 3.8: Viscotek TDAmax Triple Detection SEC System by Malvern

Table 3.7: SEC analysis parameters

Mobile phase	NMP with 0.03M LiBr
Column	2 x G-MBLMW-3078
Flow rate	0.5 mL/min
Injection volume	100 µL
Column/Detector Temperature	60ºC
Concentration	~ 5.00 mg/mL
Standard	Polystyrene
Method	Triple Detection

The sample was analyzed in NMP (with 0.03M lithium bromide) at a temperature of 60ºC and concentrations of 5.04 mg/mL. The molecular weight was determined using the light scattering and refractive index detectors. The intrinsic viscosity was measured by the viscometer and hydrodynamic radius was calculated from the product of the weight average molecular weight (Mw) and the intrinsic viscosity.

3.4 Evaluation of Synthesized and Commercial PPDs

The synthesized and commercial PPDs were evaluated for their effectiveness in reducing pour point, WAT, viscosity and yield stress values. Two waxy crudes from Peninsular Malaysia Operation (PMO) fields, Crude A2 and Crude A6, were heated to 90°C for approximately 1 hour to remove any thermal and shear history associated with the sample.

Then the conditioned crudes were dosed with PPDs in three different concentrations (300, 500 and 1000 ppm) and were thoroughly mixed to ensure homogeneity prior to laboratory analyses including rheological study by Haake Rheostress 6000 and morphology study by AFM.

The pour point and WAT analysis conducted on the treated crudes are presented in Appendix VII and Appendix VIII, respectively.

3.4.1 Rheological Study

Rheology describes the deformation of a body under the influence of stresses. Viscosity and yield stress were determined using Haake RheoStress 6000 (Figure 3.9a).

3.4.1.1 Viscosity

In order to obtain a representative sample for testing and to remove any thermal and shear history associated with the sample, the crude oil sample was heated to 90°C in a closed container for approximately 1 hour and thoroughly mixed to ensure homogeneity. Approximately, 9 mL of sample was required to fill the annular gap between cup and rotor to its upper rim (Figure 3.9b). The cup was then closed as in Figure 3.9c before the sample was heated up to 90°C and then cooled to 20°C at the cooling rate of 1 ºC/min with applied shear rates of $30s^{-1}$, $500s^{-1}$ and $1500s^{-1}$. The apparent viscosity data were recorded during the cooling process.

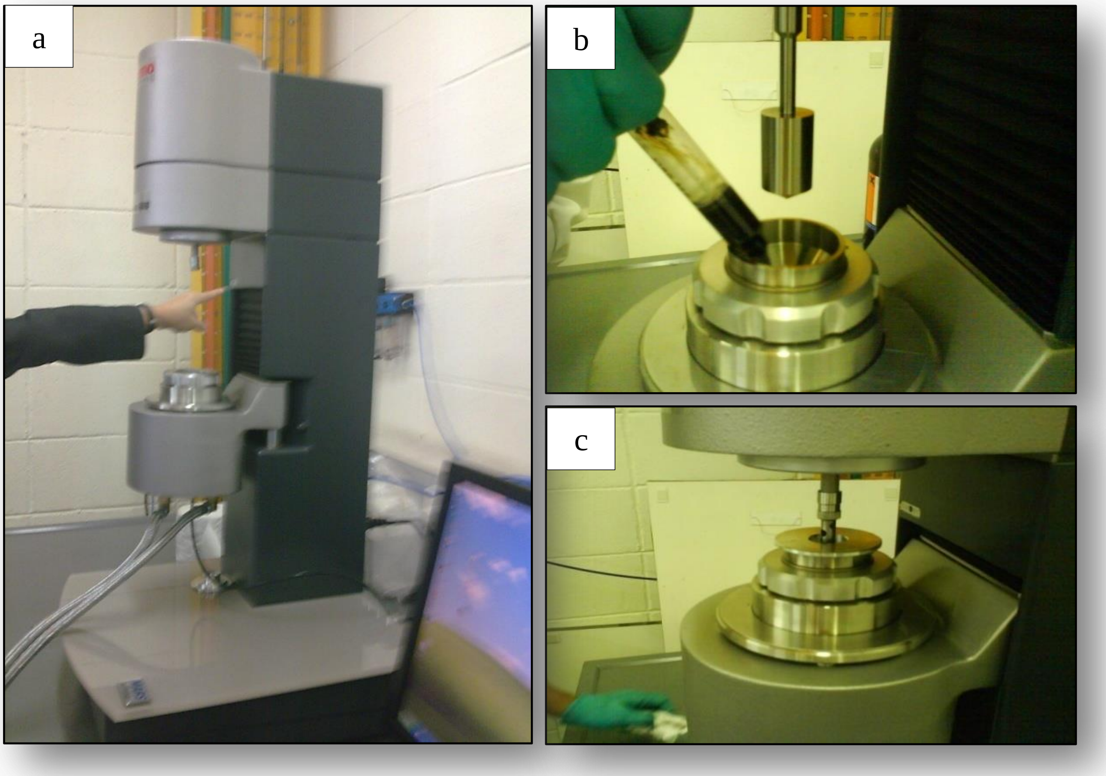


Figure 3.9: a) Haake Rheostress 6000, b) Filling the sample c) Closed cup

3.4.1.2 Yield Stress

Yield stress measurement was conducted by heating the crude oils to 90°C and then cooling them to 20°C at the cooling rate of 1 ºC/min with shear rate of 100s^{-1} . Once the temperature reached 20ºC, a high shear rate of 1000 s^{-1} was applied for 1 hour to destroy the gel formed. Then the shear rate was increased from 1 s^{-1} to 1000s^{-1} at 20°C within 3 minutes. The shear stress data were then recorded.

3.4.2 Atomic Force Microscopy (AFM)

In AFM imaging procedure, the samples were gently pressed between freshly cleaved mica sheets, and the surface studies were performed on flattened surface after a removal of mica sheets. No heating was applied.

The imaging was performed in oscillatory amplitude modulation mode with simultaneous recording of phase images. Although in this mode the tip-sample forces are typically minimized in case of oil samples the forces were tentatively elevated for tip to penetrate an amorphous material and to get high-contrast phase images.

The phase images best present the crystalline domains in these samples, which can be recognized by a particular shape and brighter contrast. The morphologies were obtained using Agilent 4500 AFM, which is presented in Figure 3.10.

Figure 3.10: Agilent series 4500 AFM

CHAPTER 4

RESULTS AND DISCUSSION

This chapter has been organized into three main sections. General characteristics of the two waxy crudes from Peninsular Malaysia Operations (PMO), namely Crudes A2 and A6 are reported and analyzed in section 4.1. Characterization of synthesized PPDs is presented in section 4.2. Lastly, the performances of the synthesized and commercial PPDs, in terms of their applicability for improving flow assurance of Malaysian waxy crude oil, are discussed in section 4.3.

4.1 Characterization of Waxy Crudes

The rheology of crude oil is believed to be influenced by waxes, resins and asphaltenes present, as well as by the thermal and mechanical history of the crude. However, the nature, type and quantity of the waxes present, as well as their crystallization habits, influence flow properties to a large extent (Agarwal *et al*., 1989).

Each crude oil has unique molecular characteristics which are important to be considered and understood prior to the treatment with any chemicals. Key parameters of a crude oil in relation to flow assurance include WAT, pour point, SARA analysis and n-paraffin distribution.

4.1.1 Physical Properties of Waxy Crudes

WAT and the pour point temperature are good pointers to the temperature regime, in which a waxy crude oil is expected to start to show non-Newtonian behavior. Their determination is an important step in the study of rheological behavior of such systems. In fact, WAT and pour point are probably the most important flow assurance measurements for waxy crudes.

Pour point represents the lowest temperature at which the crude oil can be stored or handled without congealing in the tanks or pipelines. Usually, it is 10-20 ºC lower than the cloud point (Ajienka, 1983).

The physical properties of the Malaysian waxy crudes studied are given in Table 4.1. Both Crude A2 and Crude A6 exhibit very high pour point of 48°C and 57°C and WAT of 67.6 ºC and 68.9 ºC, respectively. The wax content for both crudes are also high at 21.0 wt % and 10.3 wt %, in which permits strong gelled networks.

Table 4.1: Physical properties of waxy crudes

No	Properties	Method	Crude A2	Crude A6
1	Density at 15^{o}C , g/cm^{3}	ASTM D5002	0.8722	0.8882
2	API Gravity	Calculated	30.1	27.8
3	WAT, ^{o}C	CPM	67.6	68.9
4	Pour Point, ^{o}C	ASTM D5853	48	57
5	Wax Content, wt %	UOP46-64	21.0	10.3
6	Asphaltene Content, wt %	ASTM D3279	0.35	0.73
7	Drop Melting Point, ºC	ASTM D127	58.8	56.4
8	SARA Saturate, wt% Aromatic, wt% Resin, wt% n-Pentane Insoluble, wt%	ASTM D2007 modified	 41.39 14.85 5.39 15.01	 42.58 17.01 5.68 11.48
9	IBP (^{o}C) 30% (ºC) 50% (ºC) 70% (ºC) FBP (ºC)	Simdist (ASTM D6352 Modified)	139.8 375.0 435.0 498.5 643.0	148.6 367.0 437.0 499.0 647.0

While the WAT and pour points of crudes A2 and A6 to augur each other, the same cannot be said about the wax contents. One would anticipate the WAT and pour point to increase with an accompanying increase in wax content. In contrast, the results indicated that there is no relationship between wax content with WAT and pour point, which is agreeing with the results reported by Rønningsen *et al.,* 1991. In addition, the results reported by Elsharkawy *et al.,* 1991 also shows no correlation between WAT and wax content.

The density at 15ºC of 0.8722 and 0.8882; API gravity of 30.1 and 27.8; and initial boiling point of 139.8°C and 148.6°C confirming the waxy characteristics of both crudes under studied.

The SARA result from Table 4.1 show high saturates contents for both crudes at 41.39 wt% and 42.58% indicating the high probability for precipitating wax. Saturates are flexible hydrocarbon molecules, which tend to cluster together and precipitate from crude oil as wax solids.

However, the aromatic content that is at moderate amount of 14.85% and 17.01% help to prevent severe deposition as aromatics are known to be good solvents for paraffinic waxes. (Hammami, 1999).

The asphaltene content of Crude A2 and Crude A6 is 0.35% and 0.73%, respectively. The role of asphaltenes during the wax crystallization has not been satisfactorily explained yet. In thermodynamic terms, asphaltenes are dispersed rather than dissolved in the crude oil matrix (Lira-Galeana and Hammami, 2000). The association with resin maintains the asphaltenes as a single phase. Once the equilibrium is disrupted broken, the asphaltenes do not interact sufficiently with the resins and start to flocculate among themselves. The flocculated asphaltenes may provide the crystallization sites for paraffins (Garcia, 2000).

4.1.2 Carbon Number Distributions by HTGC

The paraffinic contents of Crude A2 and Crude A6 were analyzed using HTGC to determine the carbon number distribution of wax. Figures A1 and A2 and Tables A1 and A2 in Appendix IX, show a carbon number distribution for both crudes with few light ends in the crudes and predominantly high n-paraffin content ranged from C18 to C35.

Paraffin waxes are composed primarily of straight-chain saturated hydrocarbons with 18 to 35 carbon atoms. Lower molecular weight waxes (C18-35) are termed as macrocrystalline waxes. Microcrystalline waxes contain a large percentage of branched and cyclic hydrocarbons with carbon numbers in the 30 to 60 range (Mansoori, 1996).

The carbon number distributions as well as the high melting points of 58.8ºC and 56.4ºC for Crude A2 and Crude A6 indicate that both crudes have macrocrystalline waxes. It has been suggested that macrocrystalline waxes are the major causes of paraffin problems in production and transportation, whereas microcrystalline waxes are the major contributor to sludge problems in vessels and tanks (Jorda, 1996; Shock *et al.*, 1955).

4.2 Characterizations of Synthesized PPDs

The synthesized PPDs are coded as PPD-A10, PPD-A12, PPD-A14, PPD-A16 and PPD-A18 based from the various chain n-alkyl alcohol used in the preparation of the alkyl acrylates in the Fischer esterification. Acrylic acid was reacted with five n-alkyl alcohols (n=10, 12, 14, 16 and 18) in 1:1 mol using sulfuric acid as catalyst.

The PPDs chemical structures were investigated by Perkin Elmer FTIR-ATR spectrometer. However, only the best of the synthesized PPDs was further characterized by SEC to determine its molecular weight, intrinsic viscosity and hydrodynamic radius.

4.2.1 FTIR-ATR Spectroscopy

The IR spectrums of synthesized PPDs are presented in Figures 4.4 (a-c). The peak around 1730 cm^{-1} indicates the presence of carbonyl group (C=O stretching in ester) in the compound. The carbonyl groups are shown at 1732.80 cm^{-1}, 1729.21 cm^{-1} and 1728.24 cm^{-1} for the synthesized PPD-A12, PPD-A14 and PPD-A16, respectively. Generally, the absorptions at 2926 - 2856 cm^{-1} are characteristics of CH2 groups in the alkyl chains, while the absorptions at 1495 cm^{-1} to 1454 cm^{-1} indicate the asymmetric vibration of carboxylic groups in the synthesized PPDs.

The broad peaks at the range of 1213.23 cm^{-1} to 1206.70 cm^{-1} in the synthesized PPDs are due to the ester C-O-C stretching, whereas the broad peaks in the range of 1160.74 cm^{-1} to 1156.9 cm^{-1} are for C-H stretching vibrations for the three synthesized PPDs. Other absorptions near 800-870 cm$^{–1}$ are due to maleimide unit presence in the chain, which are shown at 813.07 cm^{-1}, 815.79 cm^{-1} and 817.72 cm^{-1} for PPD-A12, PPD-A14 and PPD-A16, respectively.

Four available commercial PPDs were analyzed by FTIR to determine their functional groups for comparison against the synthesized PPDs. The IR spectrums of commercial PPDs are presented in Appendix X.

Comparing the functional groups present in synthesized PPDs; the carbonyl groups are shown at 1732.78 cm^{-1} and 1733.48 cm^{-1} for the commercial PPD-CB and PPD-CD, respectively but none present in PPD-CA and PPD-CC.

As with the synthesized PPDs, all four commercial PPDs have strong peaks at 2927 cm^{-1} to 2854 cm^{-1}, characteristics of CH2 groups in alkyl chains. Besides that, the absorptions in the range of 1495 cm^{-1} to 1454 cm^{-1} indicating the asymmetric vibration of carboxylic groups and the broad peaks in the range of 1160.74 cm^{-1} to 1156.9 cm^{-1} due to C-H stretching were also present in all commercial PPDs.

However, none of the commercial PPDs shows any absorption near 800-870 cm$^{–1}$ to indicate the presence of the maleimide units. As such, it is concluded that the commercial PPDs are not of the same compound of the synthesized PPDs.

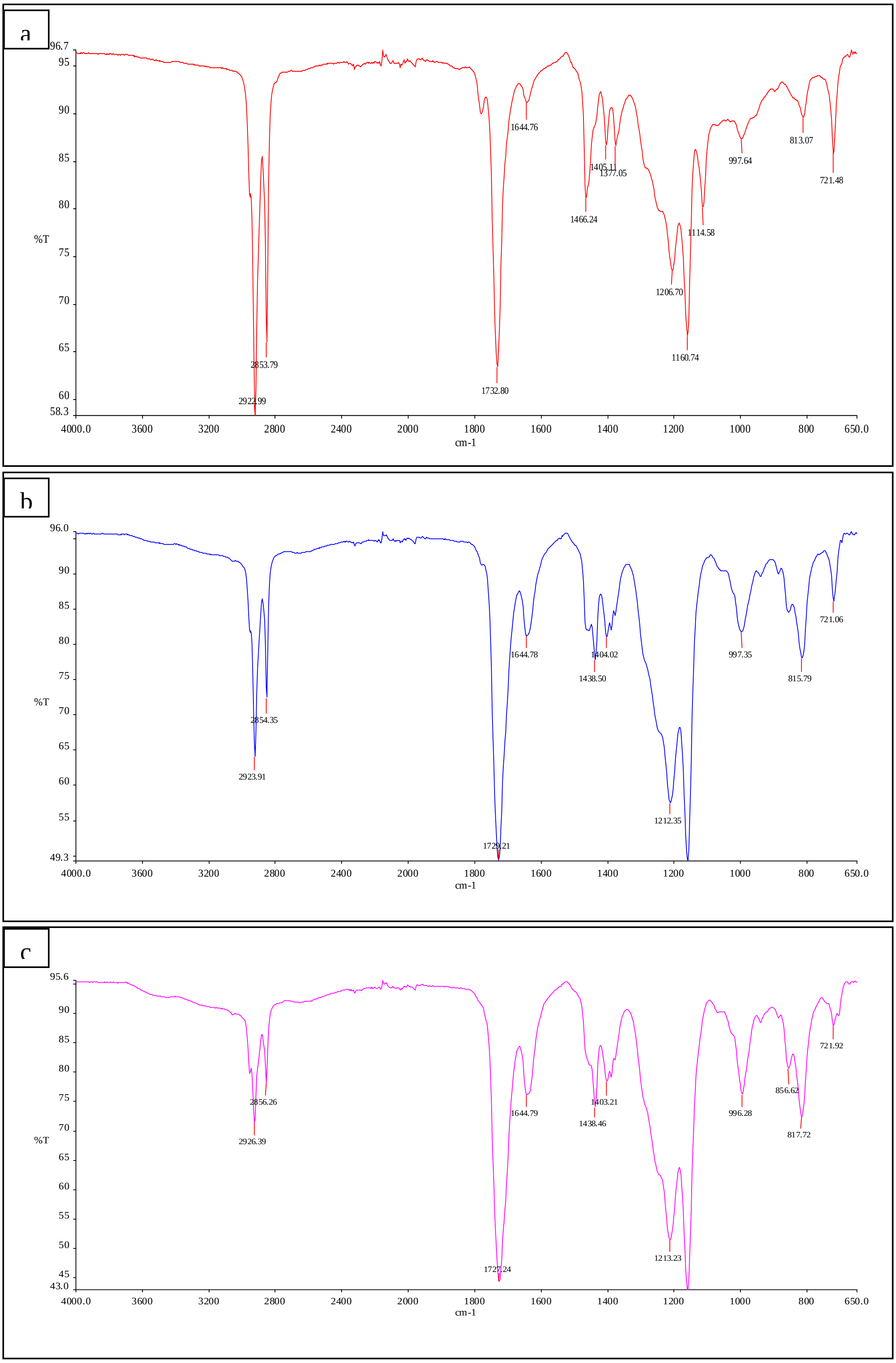


Figure 4.1: FTIR spectrum of a) PPD-A12, b) PPD-A14, c) PPD-A16

4.2.2 Molecular weight by SEC

PPD-A16 has shown the best results in reducing the pour point of both waxy crudes, hence it was selected to be analyzed further to determine its molecular weight (Mw), intrinsic viscosity (IV) and hydrodynamic radius (Rh) using Viscotek TDAmax Triple Detection SEC system by Malvern in a mobile phase of N-methyl-2-pyrrolidinone (NMP) with 0.03 M lithium bromide at a temperature of 60ºC and concentration of 5.04 mg/mL. The absolute Mw was determined using the light scattering and refractive index detectors. The IV was measured by the viscometer and the Rh was calculated from the product of the weight average Mw and the IV.

Due to the weak light scattering response of the sample, a distribution could not be accurately determined. Therefore, Malvern's Flow Injection Polymer Analysis (FIPA) method for batch analysis was employed to obtain the average Mw.

Table 4.2 presents the molecular data from the triple detector chromatograms for PPD-A16 using OmniSEC software. Results show that PPD-A16 has low molecular weight of 57,997 and hydrodynamic radius of 7.14 nm. The IV number of 0.40 dL/g for PPD-A16 was reasonable for polymeric species.

Table 4.2: Molecular data of PPD-A16 by OmniSEC software

Sample Run	**Mw**	**IV (dL/g)**	**Rh (nm)**
# 1	52994	0.3816	6.840
# 2	68300	0.4022	7.570
# 3	52698	0.4125	7.000
Average	**57997**	**0.3988**	**7.137**
SD	8924	0.0157	0.384
% RSD	15.39	3.95	5.38

Molecular weight of the PPD may affect the interaction between the polymer and the paraffin. A very short, low molecular weight polymer may not have the molecular volume to disrupt the paraffin crystals as it co-crystallizes within the paraffin matrix. A very long, high molecular weight polymer may be so large that it interacts with itself instead of the crude oil paraffin, or the polymer's solubility in the crude may be limited and actually initiate paraffin crystallization, and thus raise the crude pour point (Manka and Zieglar, 2001).

As indicated by Table 4.2, PPD-A16 is a low molecular weight polymer but still has enough molecular volume to disrupt the paraffin crystals to a certain extent as it co-crystallizes within the paraffin matrix.

4.3 Evaluation of Synthesized PPDs

The synthesized PPDs were evaluated for their effectiveness in reducing pour point, WAT, viscosity and yield stress value by laboratory analyses including rheological study by Haake Rheostress 6000 and morphology study by AFM.

4.3.1 Pour Point and WAT

Crude A2 and Crude A6 were treated with the synthesized PPDs at different concentrations so as to find the optimum concentrations that give the highest reduction of the studied parameters. The concentration of the PPD used was increased until the performance declined with more PPD dosage. Crude A2 only need up to 1000 ppm of PPD dosage as compared to Crude A6 which need higher concentration of 1200 ppm.

The PPDs were evaluated for their performance at different concentrations of 300, 500, 1000 and 1200 based from the typical concentrations applied at field. The effectiveness of the synthesized PPDs in reducing the pour point and WAT at different concentrations is shown in Table 4.3.

Table 4.3: Pour point and WAT of untreated and treated waxy crudes

Crude	PPDs Concentration, ppm	Pour Point, °C			WAT, °C		
		PPD A12	PPD A14	PPD A16	PPD A12	PPD A14	PPD A16
A2	**0**	**48**			**67.6**		
	300	48	48	45	69.1	67.6	68.4
	500	45	48	**42**	68.2	72.4	68.7
	1000	45	45	45	70.3	70.1	71.0
A6	**0**	**57**			**68.9**		
	300	57	57	57	68.7	68.4	68.4
	500	54	51	51	68.6	68.7	68.3
	1000	54	54	**45**	67.9	68.0	68.0
	1200	54	57	48	67.6	68.5	68.5

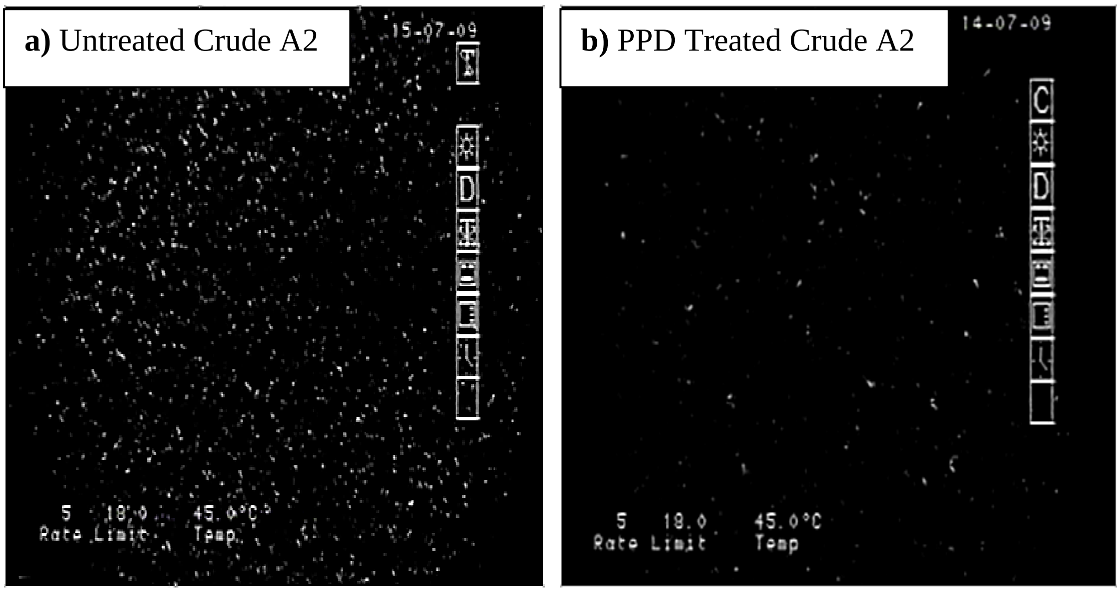
The results in Table 4.3 show that PPD-A16 has successfully reduced the pour point of Crude A2 by 6°C with 500 ppm, but further reduction to 12ºC is possible for Crude A6 with 1000 ppm but not so for Crude A2. However, the results indicate that the synthesized PPDs have no significant effect on WAT. Although WAT is an indicator of wax deposition, not all type of crystals present in WAT are similar to wax crystal. This needs more study to explain the phenomenon.

The ineffectiveness of some polymeric additives may be due to the mismatching between the numbers of carbon atoms of the pendant chains of PPDs and that of paraffin wax present in the crude oil (Soni *et al.*, 2006). It is known of wax deposition inhibitors that a good match between the length of alkyl chains of the additive and the wax components in a crude oil sample highly improves the ability to be accommodated into the wax crystals, and thereby increasing the hydrodynamic volume of the agglomerate to improve packing efficiency.

Due to the increase in hydrodynamic volume the chains cannot pack efficiently and this causes the pour point to be depressed. When the mismatch between the alkyl chain length of the wax and inhibitor is large, then there is little benefit derived from PPD incorporation. Different degrees of match between alkyl chain lengths in wax and inhibitor probably explains some of the differences in efficiency of the chemicals (Ronningsen and Karan, 2001).

The experimental results in Table 4.3 have shown that PPD-A16 is the best of the synthesized PPDs. It has the highest hydrodynamic volume contributed by the n-alkyl alcohol (n=16) as compared to PPD-A12 (n=12) and PPD-A14 (n=14).

The screen shot of the CPM images in Figure 4.2 shows the effect of PPD-A16 on the Crude A2 at below WAT (45°C). The first crystal appeared at WAT and was recorded on screen as a white dot. Below WAT the crystals of untreated Crude A2 increase as the temperature decreases to 45°C. Image of Crude A2 treated with PPD-A16 in Figure 4.2b shows the tremendous crystal decrease as compared to the untreated Crude A2 at the same temperature in Figure 4.2a. This observation indicates the pour point depression in Crude A2 treated with 500ppm PPD-A16.



a) Untreated Crude A2

b) PPD Treated Crude A2

Figure 4.2: CPM images @45°C a) treated Crude b) With 500 ppm PPD-A16

4.3.2 Crystalline Morphology by AFM

In recent years, relations between viscosity and wax crystal morphology and structure, or the precipitated wax, or composition of crude oil had been widely discussed (Pedersen & Ronningsen, 2000, Magri & Kalpakci, 1999, Kane *et al.*, 2004, Vinsintin *et al.*, 2005). However, due to complexity and irregularity of the wax crystal morphology, independent quantitative characterization of wax crystal morphology and structure was not available, and consequently, establishment of quantitative relations between apparent viscosity and wax crystal morphology, structure and composition of the crude oil could hardly be achieved.

AFM photomicrographs of crystalline morphology in Figure 4.3 (a & c) display smaller wax crystal aggregates in the untreated Crude A2 and Crude A6, respectively. The wax crystals in the untreated crudes have a corresponding homogeneous size distribution and high degree of dispersity of the particles. This will import high surface energy to untreated crude oil and thus on intense cooling easily tend to interconnect into a three-dimensional network structure, which will affect the flow behavior of waxy crude oil (Deshmukh, and Bharambe, 2007). PPD A-16 has changed the morphology of Crude A2 and Crude A6 as shown in Figures 4.3 (b & d), respectively, hence improving the flow ability of the treated crudes.

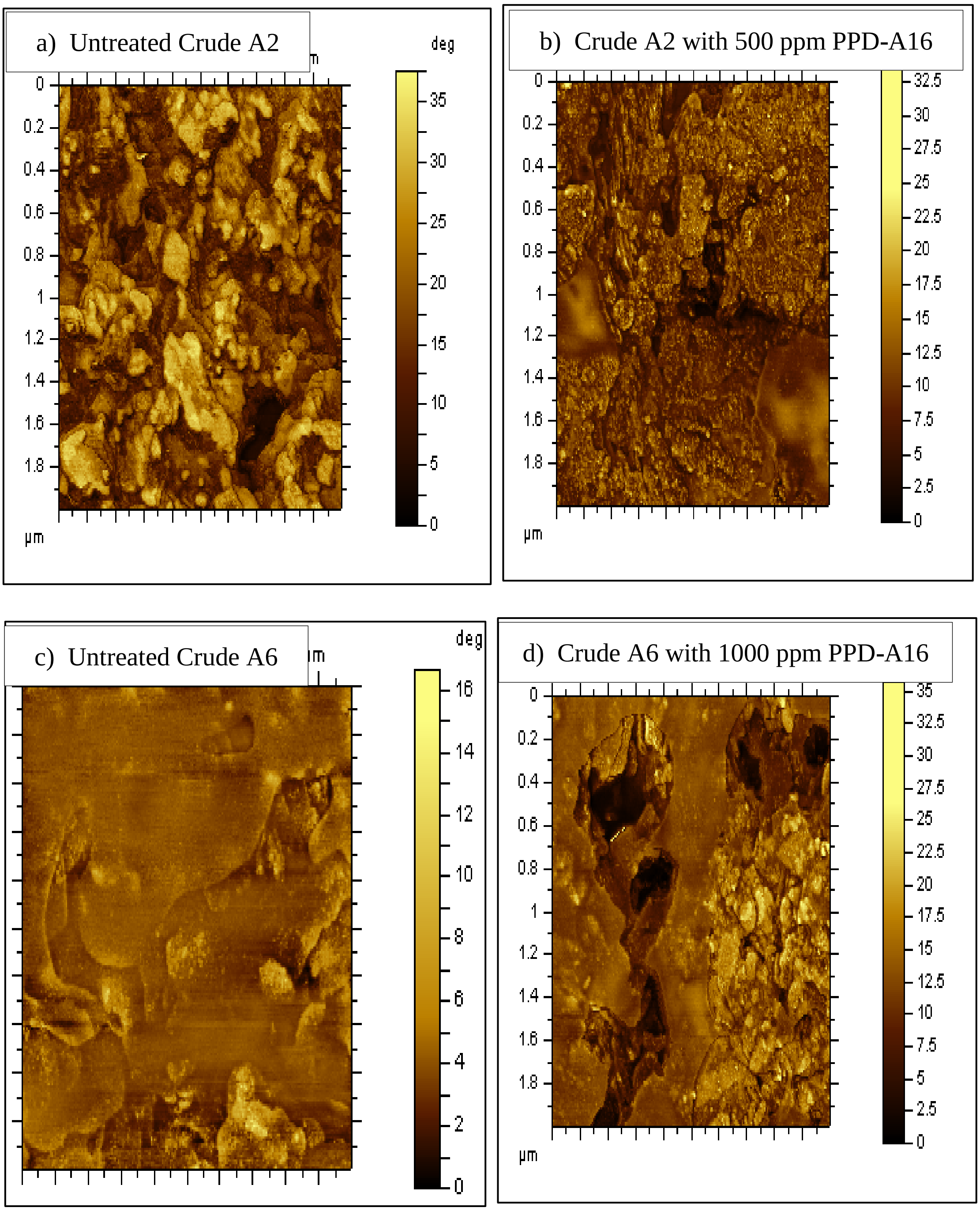


Figure 4.3: Crystalline morphology of untreated and treated waxy crudes

In the treated crudes, the single wax crystals become bigger and have tended to aggregate as clusters, which increase the zone unoccupied by the particles. This may explain the pour point reduction of Crude A2 and Crude A6 by PPD-A16 in Table 4.3 above.

The depression in pour point is mainly attributed to wax crystal modification. PPD molecules are adsorbed on the various crystals faces, thereby decreasing the interlocking forces between two nuclei of wax molecules and deforming the regular crystal growth. It is recognized that transition from plate like to spherulitic crystal structure accompanies the lowering of pour point (Manka *et al.*, 1998 and Au, 2001). This can be seen in CPM (Figure 4.2) and AFM photomicrographs (Figures 4.3).

4.3.3 Simdist by ASTM D6352 Modified

Both Crude A6 and Wax A6 (extracted through Cold Finger), were treated with PPD-A16. The untreated and treated samples were analyzed by Simdist to evaluate the effectiveness of PPD-A16 in decreasing the boiling points of both crude and extracted wax.

The Simdist chromatograms of Crude A6 and Wax A6 are presented in Figure A.4 (a & b) and Figure A.5 (a & b), respectively, in Appendix XI. The boiling points are tabulated in Table A.3 (Appendix XI).

Table 4.4 and Table 4.5 present the volume% versus temperature of the treated Crude A6 and treated Wax A6, respectively. The reduction of the temperature for volume recovery with addition of PPD-A16 are analyzed under three categories, namely light ends (10 to 30%), medium ends (40-60%) and heavy ends (70-90%).

Taking the average reduction for each end, it was observed that the medium end of Crude A6 and light end of Wax A6 have been affected the most by PPD-A16. PPD-A16 affected the wax more than the crude as indicated by the maximum average temperature reduction of 10.5 in Wax A6 and only 5.2 in Crude A6 in Table 4.4 and Table 4.5, respectively.

Table 4.4: Boiling point of untreated and treated Crude A6 with PPD-A16

Volume Recovery	Temperature, ºC		Temperature Reduction, ºC	Average Temperature Reduction, ºC
	Untreated Crude A6	Treated Crude A6		
IBP	143.5	137.5	6	
10%	248.5	252.5	(4)	1.0 (light end)
20%	311.5	310.5	1	
30%	367	365	2	
40%	410	407	3	5.2 (medium end)
50%	437	431.5	5.5	
60%	463	456	7	
70%	499	493.5	5.5	2 (heavy end)
80%	547	544	3	
90%	598	597	1	
FBP	647	645	2	

Table 4.5: Boiling point of untreated and treated Wax A6 with PPD-A16

Volume Recovery	Temperature, ºC		Temperature Reduction, ºC	Average Temperature Reduction, ºC
	Untreated Wax A6	Treated Wax A6		
IBP	172.5	150	22.5	
10%	273.5	260.5	13	10.5 (light end)
20%	328	317.5	10.5	
30%	378.5	370.5	8	
40%	415	410	5	4.7 (medium end)
50%	439.5	435.5	4	
60%	465	460	5	
70%	502	495.5	6.5	5.7 (heavy end)
80%	554.5	547.5	7	
90%	606.5	603	3.5	
FBP	654.5	654.5	0	

Upon treatment with PPD-A16, the IBP of Crude A6 has decreased by 6ºC from 143.5ºC to 137.5ºC with 4.18% reduction. The PPD-A16 has only marginally affected C17 to C37 (medium end) with the highest reduction of 1.51%.

On the other hand, the IBP of the treated Wax A6 has shown higher reduction of 13.04% where the boiling point has decreased by 22.5ºC from 172.5ºC to 150ºC. The PPD-A16 has also reduced the boiling point of C11 to C30 (medium end) quite considerably up to 15.5ºC (6.51% reduction).

4.3.4 Rheological Study

4.3.4.1 Viscosity

Figure 4.4 presents the viscosity profiles of untreated waxy crudes upon cooling from 90°C to 25°C, cooling rate of 1°C/minute and shear rates of $30s^{-1}$, $500s^{-1}$ and $1500s^{-1}$. Results show that the shear rate has considerable effect on decreasing viscosity particularly at temperatures below pour point.

The viscosity decreases with increase in temperature. Prior to approaching the pour point a steep drop is noticed which is reflected by the amount of shear applied. Higher shear rate is less steep than the lower as expected. Once it passes the pour point, the viscosity tappers gently. At this stage the effect of shear force is diminishing.

The pour points and viscosities at 45°C with different shear rates are summarized in Table 4.4. From the table it can be seen that both WAT and pour point is not affected by shear rates. The effect of shear rate on viscosity at 45°C is more obvious in crude A2 as compared to crude A6. This may be attributed to the distribution of molecular weight and nature of the wax component. From the Figure 4.4, it can be seen that Crude A2 has higher concentration of C14 to C18, higher than C18 the concentration decreases. In the case of Crude A6, it has high concentration of C15 to C29. This can be one of the reasons for the observation mentioned above

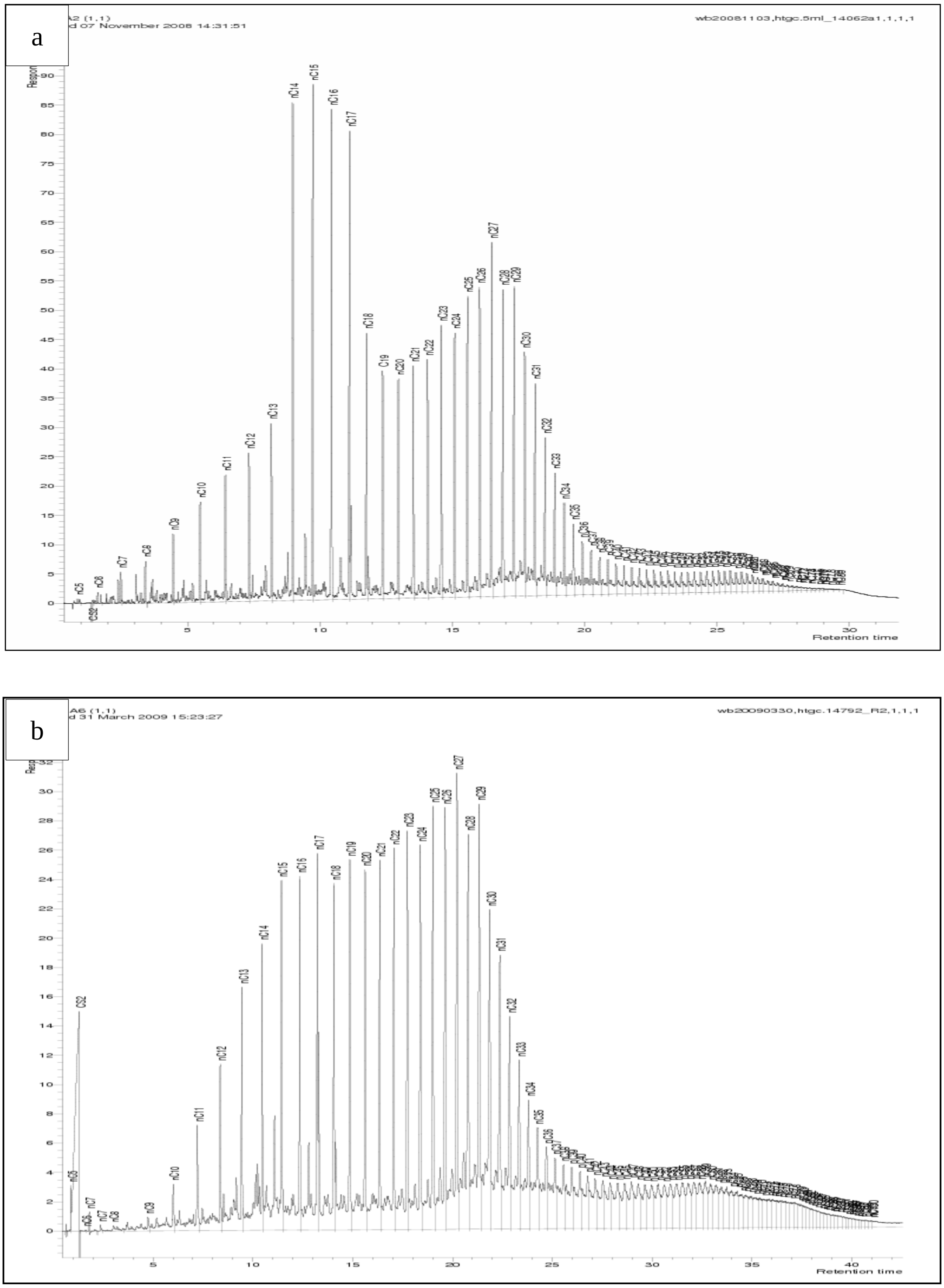


Figure 4.4: HTGC Chromatogram of a) Crude A2, b) Crude A6

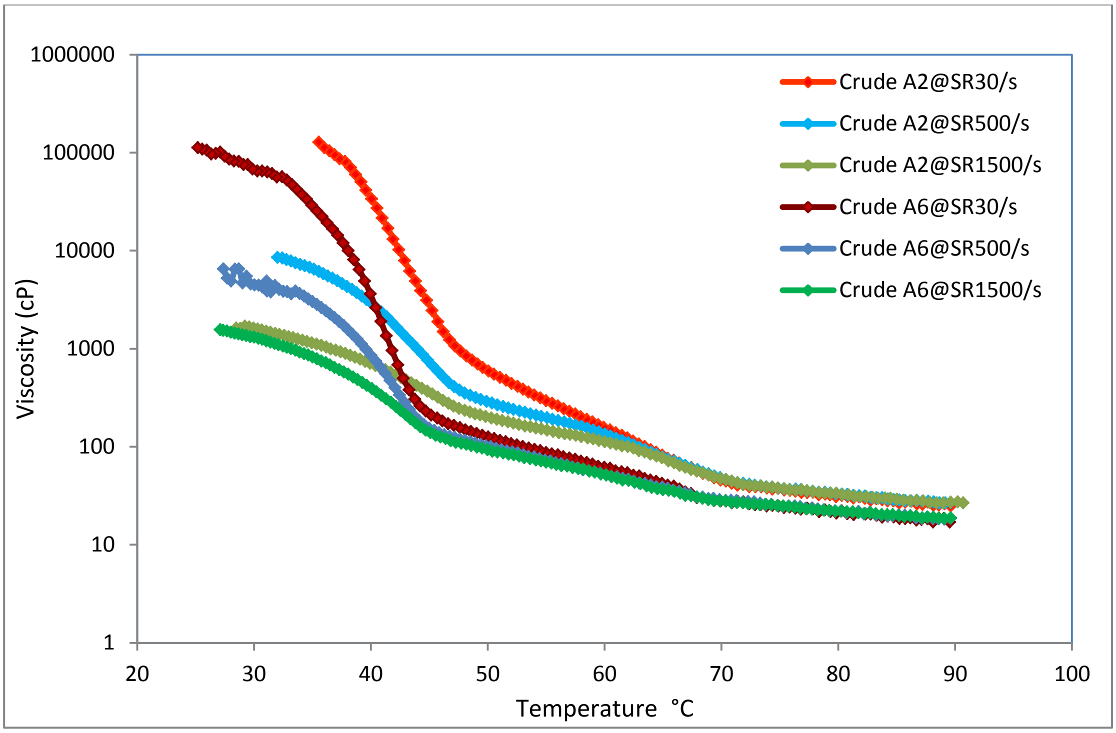


Figure 4.4: Viscosity profiles of untreated Crude A2 and Crude A6 upon cooling from 90°C to 25°C with shear rates of 30s^{-1}, 500s^{-1} and 1500s^{-1}

Table 4.6: Effect of shear rates on the rheological properties of untreated crudes

Sample	**WAT, °C**			**Pour Point, °C**			**Viscosity @ 45°C, cP**		
	30/s	**500/s**	**1500/s**	**30/s**	**500/s**	**1500/s**	**30/s**	**500/s**	**1500/s**
Crude A2	72.91	72.39	71.39	48.17	48.05	48.03	2444	671	345
Crude A6	69.92	69.34	69.31	46.13	45.86	45.11	211	155	139

Above the pour point the waxy crude oil behaves like a typical homogeneous isotropic liquid with Newtonian character. Just below the pour point, the amount of dissolved wax starts to attain its saturation limit, forming a solid solution in the crude, which leads to abrupt increase of viscosity (El-Gamal *et al.,* 1998).

The performances of the synthesized PPDs were evaluated with Crude A2 and Crude A6. However, Crude A2 was no longer available during the comparison study of the synthesized PPDs against four commercial PPDs.

Rheological curves of Crude A2 beneficiated with 500 ppm of synthesized PPDs are plotted in Figures 4.5. The rheological curves of Crude A6 beneficiated with 1000 ppm of synthesized and commercial PPDs are plotted in Figure 4.6. The graphs show that PPD-A16 have reduced the viscosities of Crude A2 and Crude A6 by 35% and 37%, respectively as compared to the original viscosity, at 45°C with applied shear rate of $500s^{-1}$ which represents field operating conditions.

The effect of PPD-A16 on Crude A2 and Crude A6 is more prominent than other PPDs as indicated by the viscosities reduction of the waxy crudes. The higher dispersing activity of these PPDs may be due to the combined effect of carbonyl oxygen of the maleic anhydride and polarity exerted by an imide group in the structure (Deshmukh and Bharambe, 2007). On the other hand, the viscosity increased by other PPDs suggest that the inhibitors, probably by some kind of steric hindrance, “inactivate” wax components within a certain range of molecular weight by preventing them from building of network structures (Pedersen *et al.,* 2003).

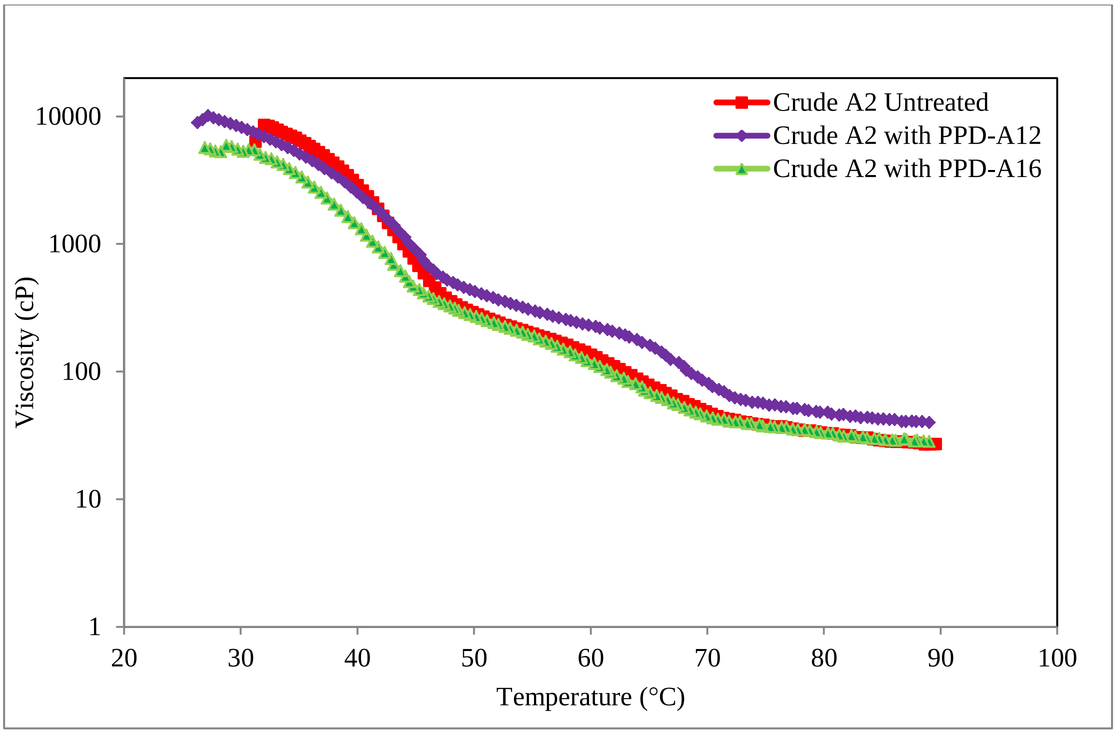


Figure 4.5: Viscosity profiles of Crude A2 with 500 ppm synthesized PPDs upon cooling from 90°C to 25°C with shear rates of 500s^{-1}

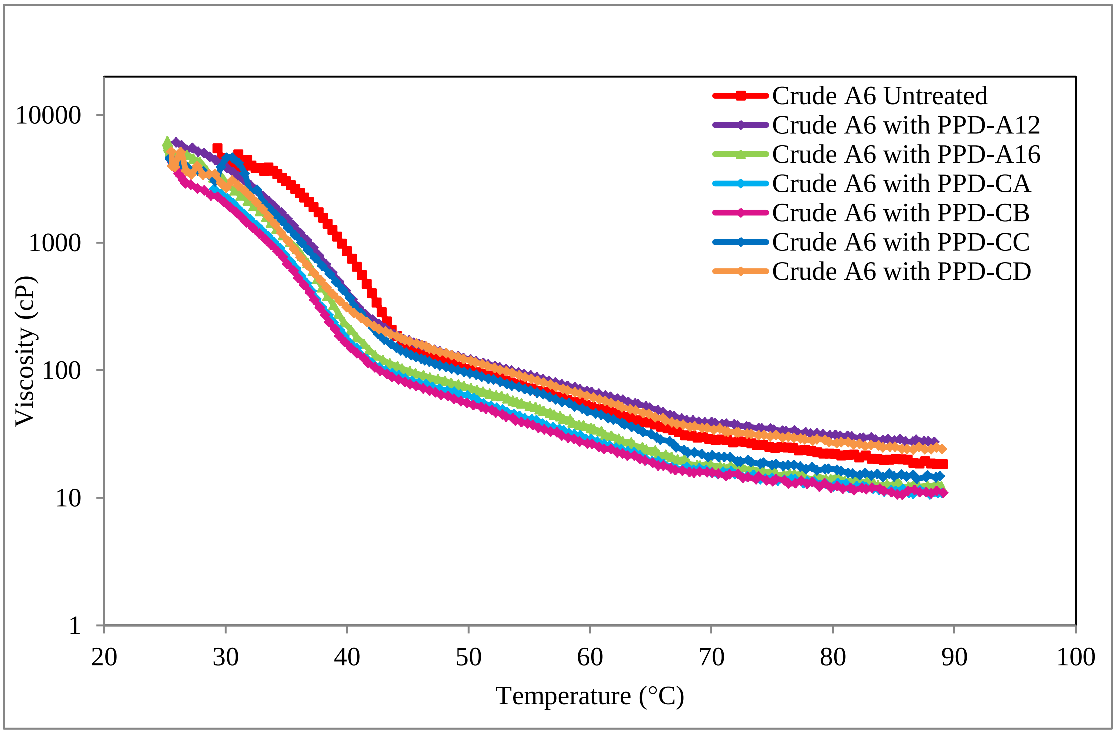


Figure 4.6: Viscosity profiles of Crude A6 with 1000 ppm PPDs upon cooling from 90°C to 25°C with shear rates of 500s^{-1}

Table 4.7: Rheological properties of waxy crudes with synthesized and commercial PPDs at 500s^{-1}

Sample	**WAT, °C**	**Pour Point, °C**	**Viscosity @ 45°C, cP**
Untreated Crude A2	71.88	48	671
Crude A2 with 500 ppm PPD-A12	72.86	47	820
Crude A2 with 500 ppm PPD-A16	70.91	45	437
Untreated Crude A6	69.84	45	155
Crude A6 with 1000 ppm PPD-A12	68.97	44	171
Crude A6 with 1000 ppm PPD-A16	69.07	43	98
Crude A6 with 1000 ppm PPD-CA	68.55	43	83
Crude A6 with 1000 ppm PPD-CB	68.57	42	78
Crude A6 with 1000 ppm PPD-CC	68.15	42	131
Crude A6 with 1000 ppm PPD-CD	68.64	42	168

Data in Table 4.5 shows that all studied PPDs only marginally influence the WAT and pour point, whereas, the majority has a pronounced effect on viscosity. PPD-A16 has reduced the viscosity of Crude A2 by 35% and Crude A6 by 37%. However, PPD-A12 has increased the viscosity of Crude A2 and Crude A6 by 22% and 10%, respectively.

Due to the insufficiency of Crude A2, only Crude A6 was evaluated in comparing the performance of the synthesized PPDs with the commercial PPDs to reduce the viscosity. PPD-A16, PPD-CA and PPD-CB have significantly reduced the viscosity of Crude A6 by 37%, 46% and 50%, respectively, at 45°C with applied shear of $500s^{-1}$ with cooling rate of 1°C/min. However PPD-CC has only marginally reduced the viscosity by 15% and PPD-CD has increased the viscosity of Crude A6 by 8%.

3.4.1.2 Yield Stress

Yield stress is an important variable in the petroleum industry to compare the strength of deposits and represents the amount of stress that needs to be applied in order for the forces between the wax crystals to be overcome, causing the gel to break (Chang *et al.,* 1999). By definition, yield stress, τo, is the limiting stress below which a sample behaves as a solid. The yield stress is a function of the cooling rate, the stress applied to the oil and the temperature at which the stress is applied. The yield stress does not have to be directly correlated to the pour point and/or gelation temperature: the pour point and the gelation temperature measure at what temperature the gel forms, not how strong the gel is (Senra, 2009).

Figures 4.7 and 4.8 show the effect of PPD-A16 on yield stress of Crude A2 and Crude A6, respectively. The yield stress results are summarized in Table 4.6.

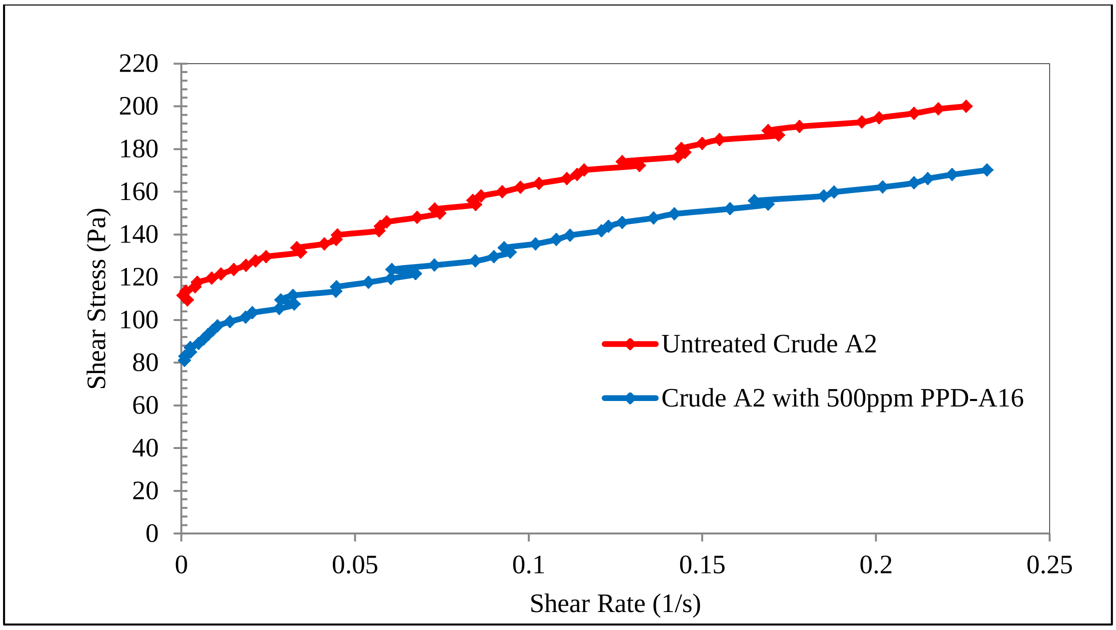


Figure 4.7: Rheogram of Crude A2 with and without PPD-A16 treatment at 45°C

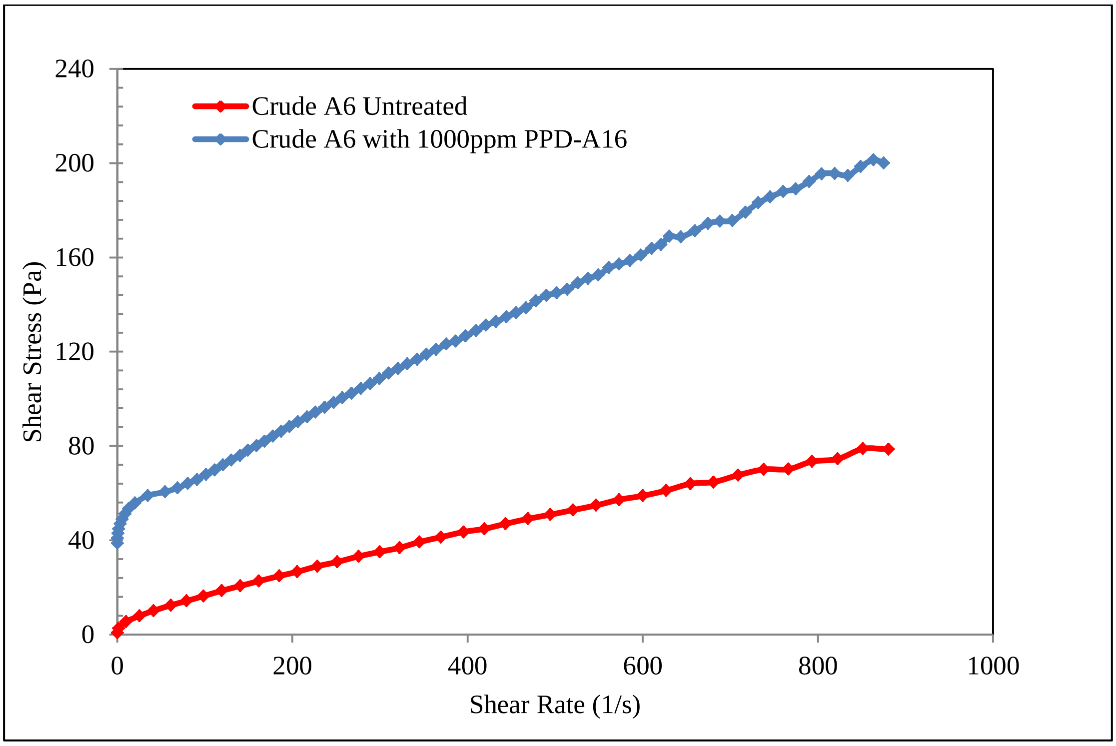


Figure 4.8: Rheogram of Crude A6 with and without PPD-A16 treatment at 54°C

PPD-A16 has reduced the yield stress of Crude A2 from 109 Pa to 81 Pa (26%) but has drastically increased the yield stress of Crude A6 from 3 Pa to 43 Pa. Richter *et al.*, 1997 and Monkenbusch *et al.*, 1994 explained this effect. At 45 °C, this polymer additive becomes insoluble in crude oil and forms aggregates, which precipitate out from the crude along with wax crystals without being properly adsorbed on the surface. Soni *et al.*, 2006 added that the pendant chains of polymers interlock into one another like a zipper. Now the polymer molecules cannot slide over one another which results in an increase in viscosity and yield value of the crude oil.

Table 4.8: Yield stress of waxy crudes untreated and treated with PPD-A16

Sample	**Temperature, °C**	**Yield Stress, Pa**	**Yield Stress Difference, %**
Crude A2 Untreated	45	109	26
Crude A2 with 500 ppm PPD-A16	45	81	
Crude A6 Untreated	54	3	(93)
Crude A6 with 1000 ppm PPD-A16	54	43	

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

In a search of effective chemical additives for improving the flow of waxy crudes, five polymeric additives were synthesized and characterized. Only three of the synthesized PPDs were evaluated on two Malaysian waxy crudes in terms of their performance to depress the pour point and to reduce the WAT, viscosity and yield stress of the studied waxy crudes. The other two synthesized PPDs, namely PPD-A10 and PPD-A18 were not evaluated further based on their FTIR results indicating of contaminations.

The obtained results have indicated that the shear rate has a noticeable effect in decreasing viscosity particularly when the temperatures is below the pour point, whereas the viscosity tends to be stable at higher shear rates (Figure 4.4).

PPD-A16 has the best efficiency for the studied waxy crudes with optimum dosages of 500 ppm for Crudes A2 and 1000 ppm for Crude A6. PPD-A16 has reduced the pour point temperature of Crude A2 by 6°C (12.5% reduction) at 500 ppm and Crude A6 by 12°C (21% reduction) at 1000 ppm dosage. It has reduced the viscosities of Crude A2 and Crude A6 at 45°C and $500s^{-1}$ by 35% and 37%, respectively. PPD-A16 has successful reduced the yield stress of Crude A2 from 109 Pa to 81 Pa with 26% reduction (Figure 4.7) but drastically increase the yield stress of Crude A6 with 93% increment (Figure 4.8).

WAT was only marginally influenced by the PPDs; however, PPD-A16 has drastically reduced the total numbers of wax crystal at 45ºC (Figure 4.2). The crystal morphology of the treated waxy crudes has also been changed and tends to aggregate in clusters which increased the hydrodynamic volume previously unoccupied by the wax particles (Figure 4.3).

The comparison study with commercial PPDs has indicated that only two of the commercial PPDs have shown better efficiency than PPD-A16. PPD-CA and PPD-CB have significantly reduced the viscosity of Crude A6 by 46% and 50%, respectively, at 45°C and $500s^{-1}$. However PPD-CC has only marginally reduced the viscosity by 15% and PPD-CD has increased the viscosity of Crude A6 by 8%.

The flow assurance is overall improved when the pour point is depressed as well as when the viscosity and yield stress are reduced.

5.2. Recommendations

This research needs to be advanced to develop effective wax control chemicals (WCC) for problematic waxy crudes and to streamline the chemical treatment selection process for production engineers.

A theory/model which can predict performance of WCC based on oil properties need to be developed as to produce an effective pre-screening tool and rapid identification for selection of product type for problematic oils.

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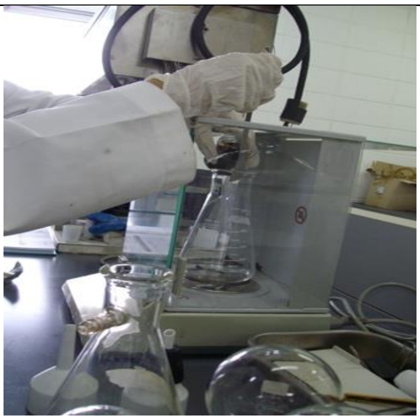
APPENDICES

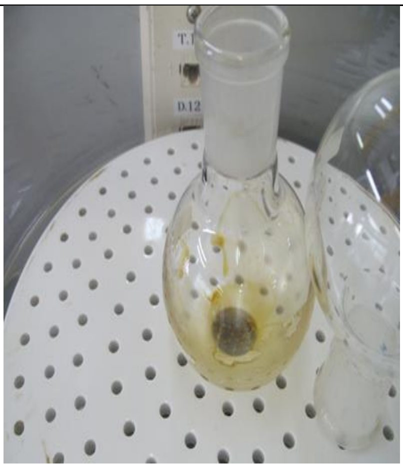
Appendix I: Publications

1. 8th Biannual Postgraduate Symposium (9 January 2009)
2. 9th Biannual Postgraduate Symposium (3 July 2009)
3. Petroleum Engineering Forum, “Evaluation of PPD for Offshore Production of Waxy Crude, KL Convention Centre (October 2009)
4. 10th Biannual Postgraduate Symposium (18 February 2010)
5. 11th Biannual Postgraduate Symposium (8 November 2010)
6. SPE Applied Technology Workshop: Assuring Flow from Pore to Process, “Indigenous Development of Pour Point Depressants (PPDs) for Malaysian Waxy Crudes”, 20-23 March 2011, Langkawi

Appendix II: Wax Content Analysis

No	Figures	Procedures
1		• A 100 mL round bottom flasks were dried in an oven @105ºC for 30 minutes then in a dessicator for about an hour. • The flask was weighed to the nearest 0.1 mg
2		The sample was weighed in the range of 1-2g.
3		• 200 mL of petroleum spirit (40/60) and 4 spoons of bole white were added into the sample. • The mixture was mixed thoroughly.

4		The solution was filtered and the residue was dissolved with hot petroleum spirit.
5		• The solution was poured into a round bottom flask. • The petroleum spirit was evaporated by rotary evaporator.
6		• The clarified residue was dissolved with 100 mL of acetone-petroleum spirit (75:25) mixture. • The solution was chilled in the water:glycol (50:50) bath @-17˚C for an hour.

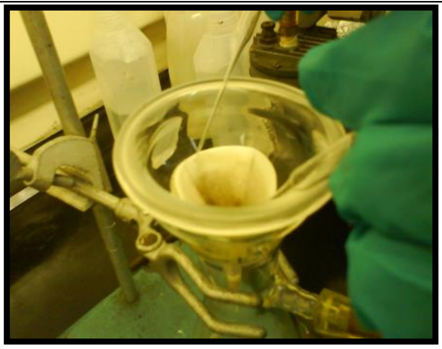
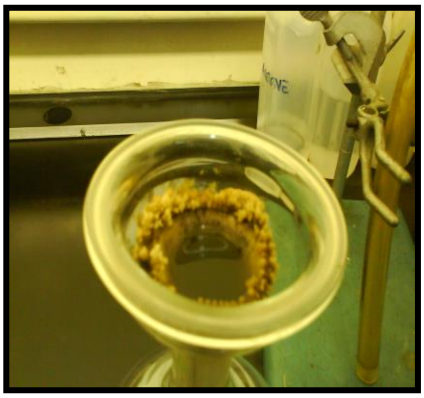
7		- The solution was filtered through a cold filter funnel with 47 mm filter paper. - The wax was subsequently washed from filter paper into the flask
8		- The solution was poured into a pre-weighed round bottom flask. - The acetone- petroleum spirit mixture was evaporated by rotary evaporator
9		- The precipitated wax was dried in the oven @105ºC for an hour followed by the dessicator for another hour. - The wax was weighed until constant weight was obtained.
10	Wax content was calculated using the following formula: $Wax\ content, wt\% = \frac{wt\ of\ dried\ sample - empty\ flask}{wt\ of\ sample} \times 100$	

Appendix III: Determination of SARA Content

Step 1: Loss on Heating at 100^{o}C

No.	**Figures**	**Procedure**
1		• 0.50 g sample was weighed in a pre-weighed beaker • The sample was dried in the oven @100ºC for 5 hours, cooled in the dessicator for 10 minutes and weighed to a constant weight (±0.001g)
2	$Volatiles, wt\% = \frac{wt\ of\ original\ sample - wt\ of\ dry\ sample}{wt\ of\ original\ sample} \times 100$	

Step 2: n-pentane Insoluble

No.	**Figures**	**Procedure**
1		• The dried sample from Step 1 was transferred to a round-bottom flask • 200 mL of n-pentane was added to the flask. • The mixture was refluxed for 1 hour to ensure complete dissolution of n-pentane soluble fraction
2		The flask was covered with aluminum foil and kept overnight in the dark.
3	 Filtration (First Half Hour)  Filtration (Last Half Hour)	The residue was filtered through a pre-weighed Whatman No.1 filter paper using vacuum to increase the rate of filtration process.

4	The entire residue was transferred onto the Whatman No. 1 filter paper using small portions of n-pentane and rinsed with 30 mL n-pentane.
5	The filtrate was preserved for determination of saturates, aromatics and resins.
6	The filter paper was dried and weighed to a constant weight.
7	$n - pentane\ insolubles, wt\ \% = \frac{wt\ of\ residue}{wt\ of\ sample} \times 100$

Step 3: Saturates Contents

No.	Figures	Procedure
1		• 40 g of silica gel was weighed and heated in an oven @100℃ for 3 hours for the activation of the silica gel. • After cooling the silica gel in a dessicator, the silica gel was packed in a column.
2		• Small portion of n-pentane was poured through the silica gel packed column to avoid air being trapped. • The filtrate from Step 2 was poured into the column and allowed to elute until very small portion was left above the column • The filtration flask was rinsed with 3-4 small portions of n-pentane, and the washings were poured into the silica-packed column.

3		• After elution of washings, the column was further eluted with n-pentane until the volume of eluted solution became 300 mL. • The eluted solution was collected in a pre-weighed 500 mL round-bottom flask. • The excess n-pentane was distilled off by rotary evaporator.
4	The flask was dried in an oven @105ºC, cooled in a desiccator and weighed to a constant weight	
5	$Saturates, wt\% = \frac{wt\ of\ residue}{wt\ of\ sample} \times 100$	

Step 4: Aromatic Contents

No.	Procedure
1	The column was eluted with small portions of toluene until 300 mL volume was eluted into a pre-weighed 500 mL round bottom flask.
2	The excess toluene was distilled off using rotary evaporator.
3	The flask was dried in an oven @105ºC, cooled in a desiccator and weighed to a constant weight
4	$Aromatics, wt\% = \frac{wt\ of\ residue}{wt\ of\ sample} \times 100$

Step 5: Resin Contents

No.	Procedure
1	The column was eluted with 200 mL (in small portions) of methanol-toluene (10:90) solvent into a pre-weighed 500 mL round-bottom flask.
2	The excess solvent was distilled off using rotary evaporator.
3	The flask was dried in an oven @105ºC, cooled in a desiccator and weighed to a constant weight
4	$Resin, wt\% = \frac{wt\ of\ residue}{wt\ of\ sample} \times 100$

Appendix IV: Synthesis of PPDs

Calculations

Step 1: Synthesis of the n-Alkyl acrylates

To calculate the molarity (for liquid), we used the formula:

$$M = \frac{Density}{Mw} \times \%\, of\ chemical\, purity\ \times 1000$$

For 1- Dodecanol (n12) that is in liquid form; Mw=186.34 g/mol, density=0.820

$$M = \frac{0.820}{186.34} \times \frac{98}{100} \times 1000$$

= 4.31

The amount of solution should equals to 250ml of 1 mol solution, therefore:

M_1V_1=M_2V_2

$$Vol\ of\ n12, V1 = \frac{(1)(250)}{4.313}$$

= 57.97 mL

The calculation was the same for acrylic acid which was in liquid form:

$$M = \frac{1.05}{72.06} \times \frac{99.5}{100} \times 1000$$

= 14.50

$$Vol\ of\ acrylic\ acid, V1 = \frac{(1)(250)}{14.4983}$$

= 17.24 m

Thus, 57.97 mL of 1-Dodecanol (n18) was reacted with 17.24 mL of acrylic acid with a few drops of concentrated sulfuric acid as catalyst.

The calculation for solid alkyl alcohols was different from liquid alcohols.
For 1-Octadecanol (n18) with Mw=270.50 g/mol.

$$x\ g\ n18 = \ 75\ mL\ \times \frac{270.50\ g}{1000\ mL}$$

$$= \mathbf{20.29\ g}$$

The volume of acrylic acid was calculated using the following relationship;

$$Vol\ of\ acrylic\ acid, V1 = \frac{(1)(75)}{14.4983}$$

$$= \mathbf{5.17\ mL}$$

Therefore, 20.29 g of 1-Octadecanol was reacted with 5.17 mL of acrylic acid with a few drops of concentrated sulfuric acid as catalyst. The solution was diluted in distilled water and made up to a total volume of 75 mL.

The same calculation was done for n14 and n16.

Step 2: Preparation of anhydride copolymer

The n-alkyl acrylates and maleic anhydride were reacted in 1:1 mole ratio in dry benzene under nitrogen atmosphere using benzoyl peroxide as initiator (1 wt%).

The volume of n12 after step 1 was 53 mL and its density was 0.8481. Mass of n-alkyl acrylates was calculated using the following relationship;

$$Density = \frac{mass}{volume}$$

Mass of n12 = Density X Volume

= 0.8481 X 53 mL

= **44.95 g**

$$Mw = \frac{mass}{mol}$$

$$mol = \frac{44.95\ g}{215\ g/mol}$$

= 0.21 mol n12

Mw of Maleic Anhydride = 98.06 g/mol

Mass = mol x Mw

= 0.21 mol X 98.06 g/mol

= **20.50 g Maleic Anhydride**

Benzoyl Peroxide used was 1% from the total weight of n12 and Maleic Anhydride

Total weight = 44.95 g + 20.50 g = 65.45 g

Mass needed = 1% X 65.45 g = **0.65 g Benzoyl peroxide**

Step 3: Preparation of Polyimide

Weight for Anhydride copolymer of n12 = 20.08 g
Mw of anhydride copolymer of n12 = 250 g/mol.

$$mol = \frac{mass}{Mw} = \frac{20.08\ g}{250\ g/mol}$$

= 0.080 mol anhydride copolymer (n12)

Mw of hexadecylamine = 241.46 g/mol
Mass = mol x Mw
= 0.0.08 mol x 241.46 g/mol
= **19.39 g hexadecylamine**

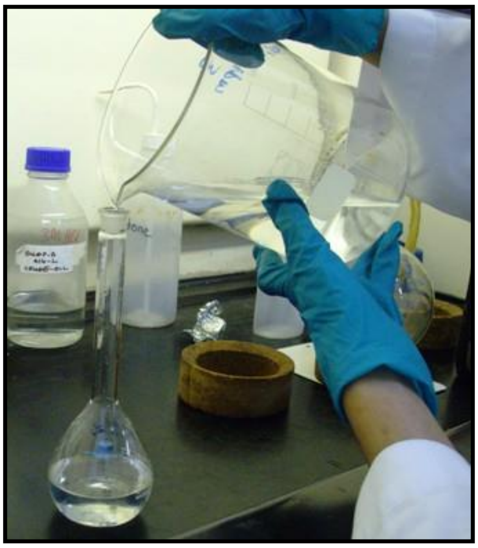
To calculate the amount of toluene, a test was done to check how much toluene was needed to dissolve an amount of hexadecylamine. We found out that 2ml of toluene was enough to dissolve 0.4g of hexadecylamine.

$$x\ mL\ Toluene = \frac{19.39}{0.4} \times 2$$

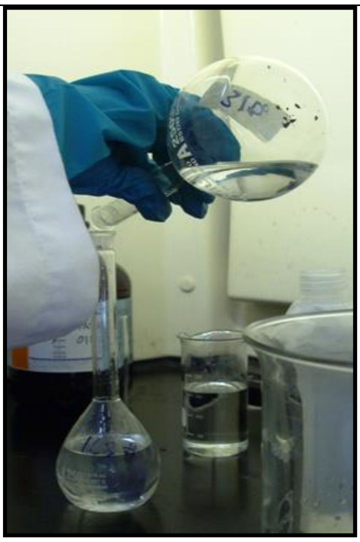
= 96.95 mL

Procedures

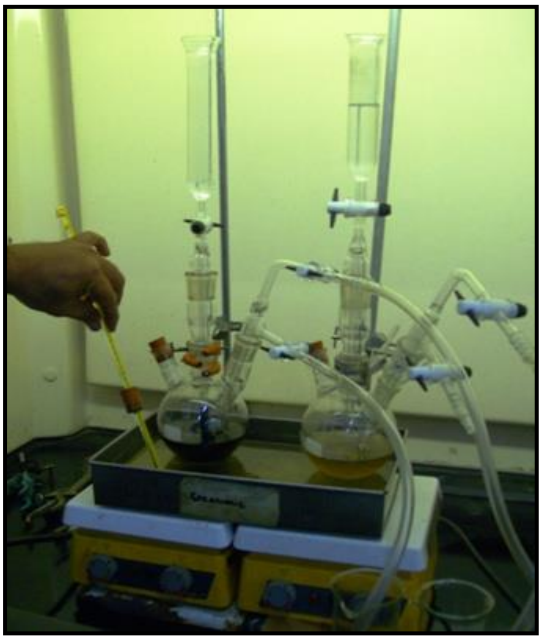
Step 1a: Synthesis of n-Decyl Acrylate (n10)

1.		a. 17.24 mL of acrylic acid was poured into a 250 mL flask. The solution was then marked up with distilled water b. 48.21 mL of 1-Decanol was poured into another 250 mL flask. The solution was then marked up with distilled water. c. Both flasks were shaken vigorously to homogenize the solutions.
2.		a. The diluted acrylic acid and 1-decanol were poured into a round bottom flask and was mixed thoroughly. b. A few drops of concentrated H_2SO_4 were added as catalyst c. Water was separated azeotropically by Dean & Stark until there was no water increment in the receiving tube (about 3 hours). d. The solution was then kept in a dry environment. e. The process was repeated in 1-Dodecyl acrylate preparation.

Step 1b: Synthesis of n-Octyl Acrylate (n16)

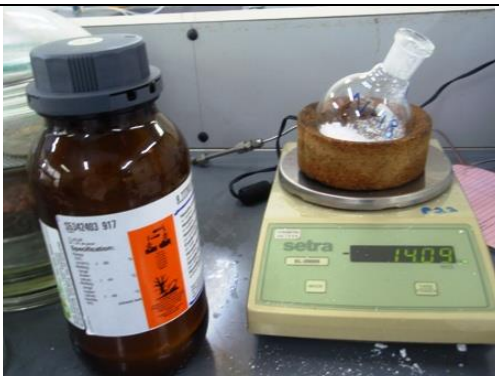
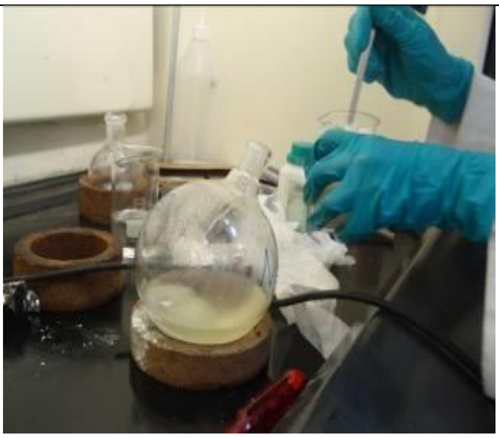
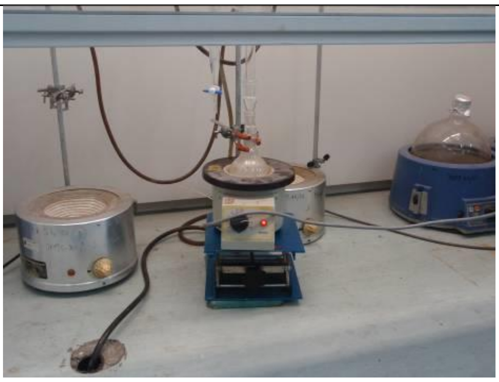
1.		a. 18.18 g Octadecanol was added into 5.17 mL acrylic acid b. The solution was marked up to 75 mL with distilled water.
2.		a. The flask was then shaken vigorously to homogenize the solution. b. A few drops of concentrated H_2SO_4 were added as catalyst.
3.		a. Water was separated azeotropically by Dean & Stark until there was no water increment in the receiving tube (about 3 hours). b. The solution was then kept in a dry environment.

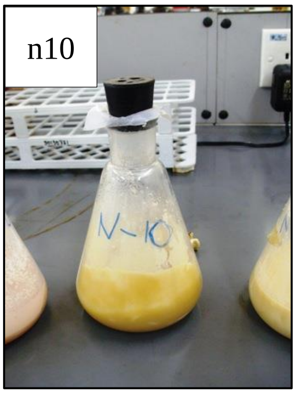
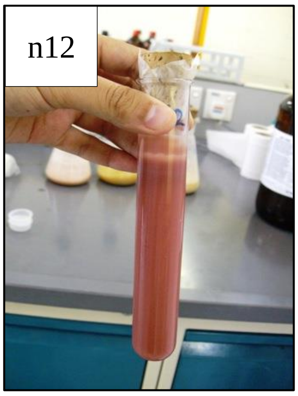
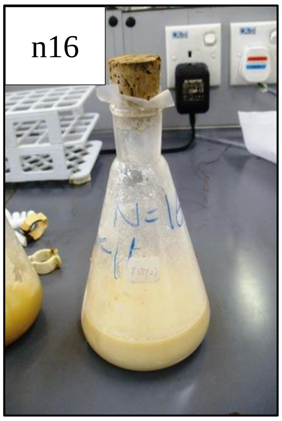
Step 2: Preparation of anhydride copolymer (n10)

1.		a. A 100 mL three-neck round flask was fitted with a condenser, a temperature controller, and a nitrogen-controlled inlet valve b. 38.47 g of n-Decyl acrylates and 19.75 g Maleic anhydride were added into the flask c. 200 mL of dry benzene and 0.58 g of benzoyl peroxide was then added into the flask.
2		a. The solution was heated at 60-70˚C with constant stirring for 7-8 hrs. b. The white oil liquid was used for the heating process.
3		a. After the reaction has completed, the solution was transferred to a round bottom flask. b. Benzene was distilled off using rotary evaporator at 60˚C under vacuum for 2-3 hours.

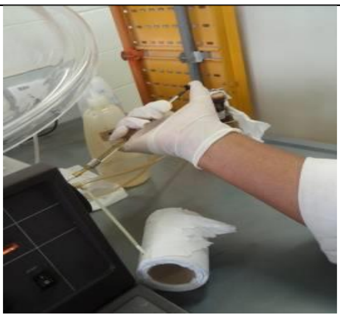
4		The flask was connected to the vacuum tube to increase the rate of filtration.
5		a. Excess amount of methanol (approximately 200 mL) was added onto the copolymer. b. The mixture was mixed thoroughly c. The filter paper was first wetted with methanol. d. The solution was then poured slowly into the flask.
6		The product was then kept inside a petri dish and kept inside the desiccator.

Step 3: Preparation of Polyimide (n10)

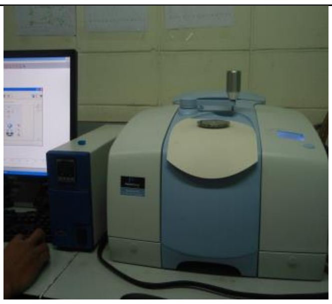
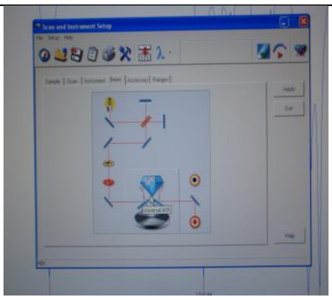
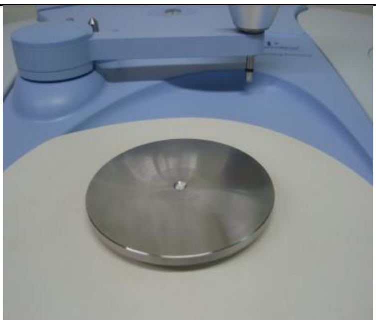
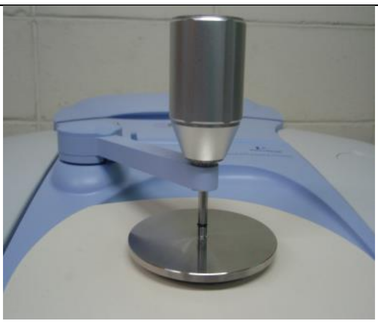
1		• 30.67 g hexadecylamine and 28.703 g of anhydride copolymer were weighed into round bottom flask.
2		153.35 mL in excess Toluene was added to the hexadecylamine and anhydride copolymer mixture.
3		The solution was heated below Toluene’s boiling point (110˚C) for about 10-15 hours
4		After the heating process was done, the toluene was distilled off using rotary evaporator.

5	 n10  n12 Final products  n14  n16  n18

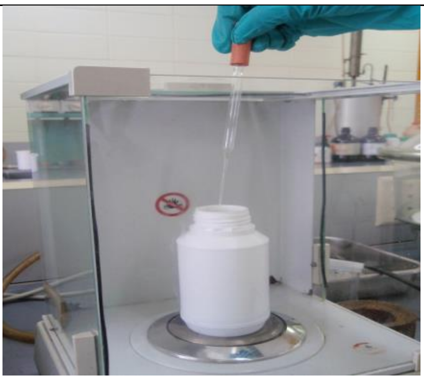
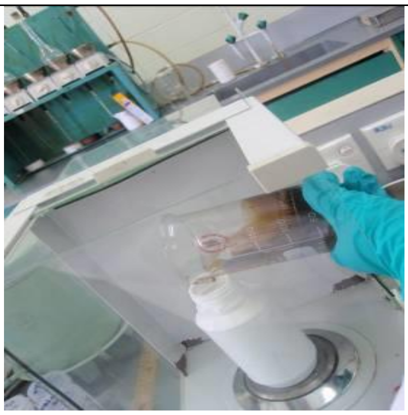
Appendix V: Density Test for n-Alkyl Acrylates

No	Figures	Procedures
1		The equipment was calibrated using distilled water before proceeding with the density tests on n-alkyl acrylates.
2		Using a syringe, the sample was taken until the volume in the syringe was almost full
3		• The sample was then injected into the density test equipment to fill the tube fully. • The injected sample was observed from the microscope lens to ensure that no bubble was formed inside the tube.
4		The density reading was taken from the equipment display.
5		The tube was washed with DCM every time after use.

Appendix VI: FTIR-ATR Analysis

No.	Figures	Procedure
1		• The detector was changed to Pike Heated Diamond GladiATR accessory. • The Spectrum Software was used together with this equipment.
2		A picture of big diamond on screen indicated that the detector was already in place.
3		The diamond detector was located at the center of the plate.
4		A droplet of sample was placed using small spatula into the diamond composite sample holding plate.
5		• The sample holding plate was equipped with a load to spread the sample uniformly and tightly against the diamond surface. • The scanning started when the pressure reached around 90 kPa.

Appendix VII: Pour Point Test for Treated Crudes

No.	**Figures**	**Procedure**
1		0.05 g of PPD was transferred into a mixing bottle.
2		50 mL of the heated crude was poured into the mixing bottle.
3		- The mixing bottle was put in the water bath @80˚C. - The bottle was shaken at 30 minutes interval for 3-4 times to homogenize the mixture before pouring it into the test jar.
4		- The test jar was put in the water bath at 0˚C. - When sample reached 60˚C, the test jar was tilted to 45˚ angle. - This was repeated at every 3˚C drop until the sample stop flowing. - The test tube was held horizontally for 5 sec to observe sample movement.

Appendix VIII: WAT Test for Treated Crudes

No.	Figures	Procedure
1.		The newly synthesized PPD was mixed with waxy crudes as in pour point test. .
2.		• A drop of homogenous sample was placed between the cross-polarized filters • The glass specimens were placed under the microscope on the CPM equipment. • The oil sample was placed between the cross-polarized filters
3.		• The sample was heated from 20-90˚C then cooled back from 90˚C back to 20˚C. • The record button was turned on while cooling down sample from 50-20˚C.
4.		WAT was observed on the screen as a small white dot on the screen.

Appendix IX: HTGC Results of Crude A2 and Crude A6

Table A.1: Composition of Crude A2

Component	Wt %	Component	Wt %	Component	Wt %	Component	Wt %
C9	2.63	C32	2.45	C55	0.53	C78	0.03
C10	1.63	C33	2.06	C56	0.52	C79	0.01
C11	1.79	C34	1.72	C57	0.56	C80	0.01
C12	1.96	C35	1.48	C58	0.51	C81	-
C13	2.46	C36	1.26	C59	0.51	C82	-
C14	4.77	C37	1.14	C60	0.49	C83	-
C15	5.06	C38	1.02	C61	0.47	C84	-
C16	4.41	C39	0.90	C62	0.43	C85	-
C17	4.39	C40	0.84	C63	0.38	C86	-
C18	3.20	C41	0.77	C64	0.33	C87	-
C19	2.73	C42	0.70	C65	0.31	C88	-
C20	2.35	C43	0.66	C66	0.26	C89	-
C21	2.44	C44	0.62	C67	0.22	C90	-
C22	2.45	C45	0.60	C68	0.19	C91	-
C23	2.68	C46	0.58	C69	0.17	C92	-
C24	2.70	C47	0.57	C70	0.13	C93	-
C25	3.07	C48	0.55	C71	0.10	C94	-
C26	3.28	C49	0.54	C72	0.10	C95	-
C27	3.86	C50	0.54	C73	0.07	C96	-
C28	3.89	C51	0.52	C74	0.07	C97	-
C29	3.92	C52	0.52	C75	0.06	C98	-
C30	3.58	C53	0.53	C76	0.05	C99	-
C31	3.10	C54	0.53	C 77	0.04	C100+	-
							100

Table A.2: Composition of Crude A6

Component	Wt %	Component	Wt %	Component	Wt %	Component	Wt %
C9	0.75	C32	2.70	C55	0.52	C78	-
C10	0.83	C33	2.32	C56	0.47	C79	-
C11	1.17	C34	1.95	C57	0.47	C80	-
C12	1.58	C35	1.71	C58	0.47	C81	-
C13	2.45	C36	1.41	C59	0.45	C82	-
C14	2.99	C37	1.27	C60	0.46	C83	-
C15	3.67	C38	1.13	C61	0.42	C84	-
C16	2.71	C39	1.06	C62	0.37	C85	-
C17	3.11	C40	0.95	C63	0.33	C86	-
C18	3.67	C41	0.79	C64	0.27	C87	-
C19	3.53	C42	0.73	C65	0.27	C88	-
C20	2.86	C43	0.68	C66	0.19	C89	-
C21	3.03	C44	0.70	C67	0.18	C90	-
C22	3.11	C45	0.61	C68	0.16	C91	-
C23	3.15	C46	0.58	C69	0.11	C92	-
C24	3.39	C47	0.55	C70	0.09	C93	-
C25	3.76	C48	0.57	C71	0.08	C94	-
C26	4.10	C49	0.52	C72	0.06	C95	-
C27	4.79	C50	0.54	C73	0.05	C96	-
C28	4.65	C51	0.43	C74	0.04	C97	-
C29	4.92	C52	0.48	C75	0.02	C98	-
C30	3.98	C53	0.54	C76	0.01	C99	-
C31	3.53	C54	0.56	C 77	0.01	C100+	-
							100

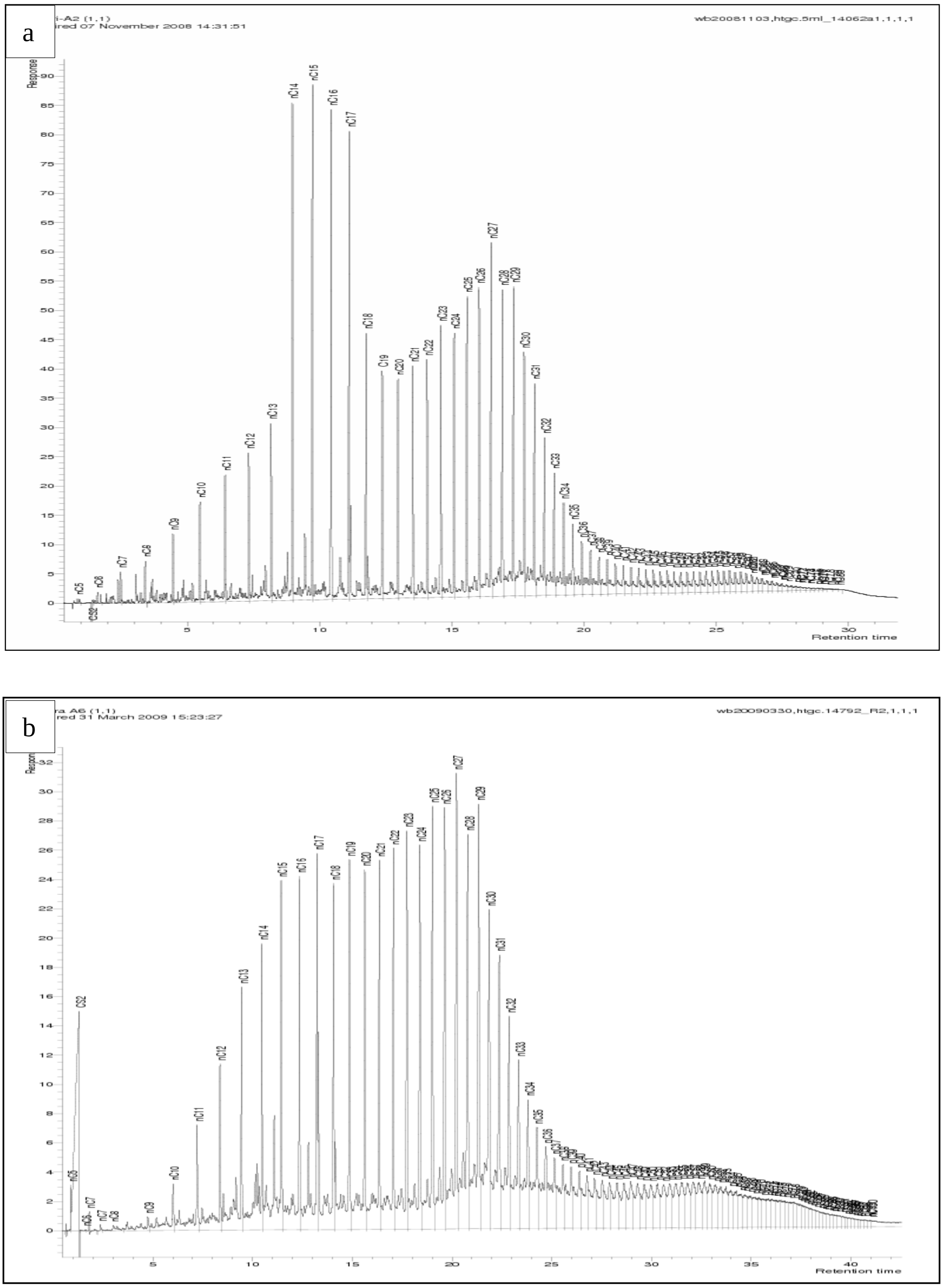


Figure A.1: HTGC Chromatogram of a) Crude A2, b) Crude A6

Appendix X: FTIR Spectrums of Commercial PPDs

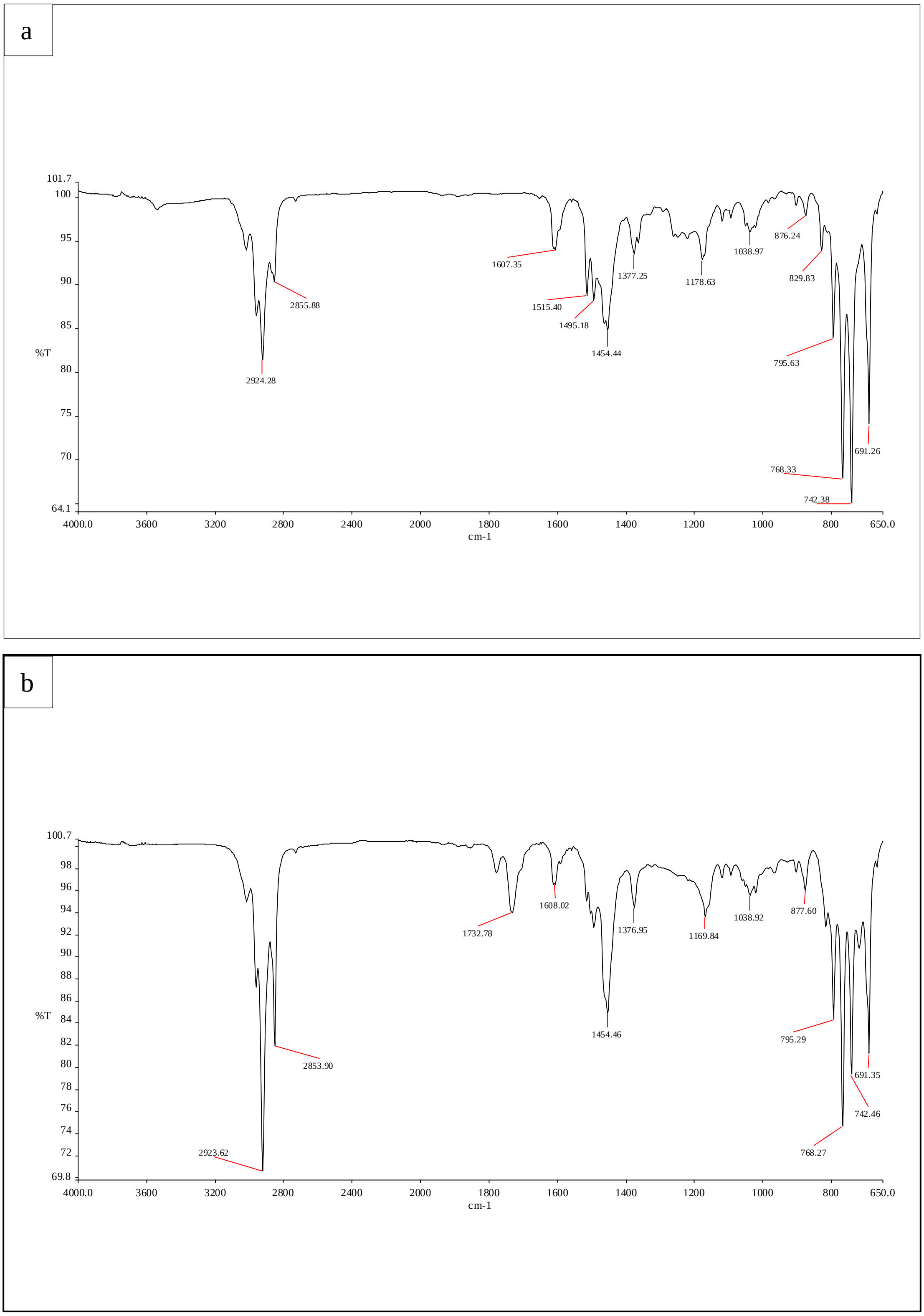


Figure A.2: FTIR spectrum of a) PPD-CA, b) PPD-CB

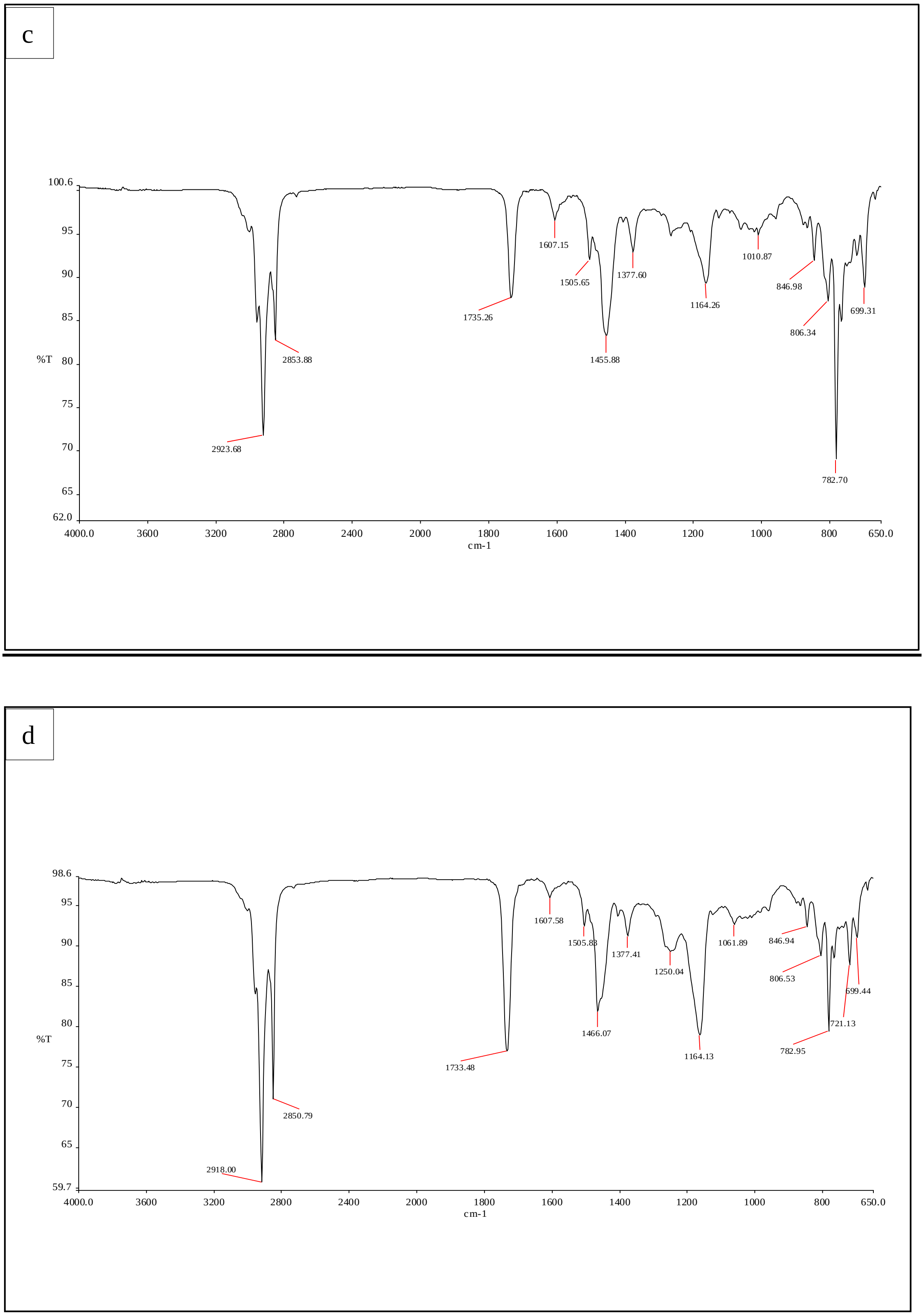


Figure A.3: FTIR spectrum of c) PPD-CC, d) PPD-CD

Appendix XI: Simdist Results of Crude A6 and Wax A6

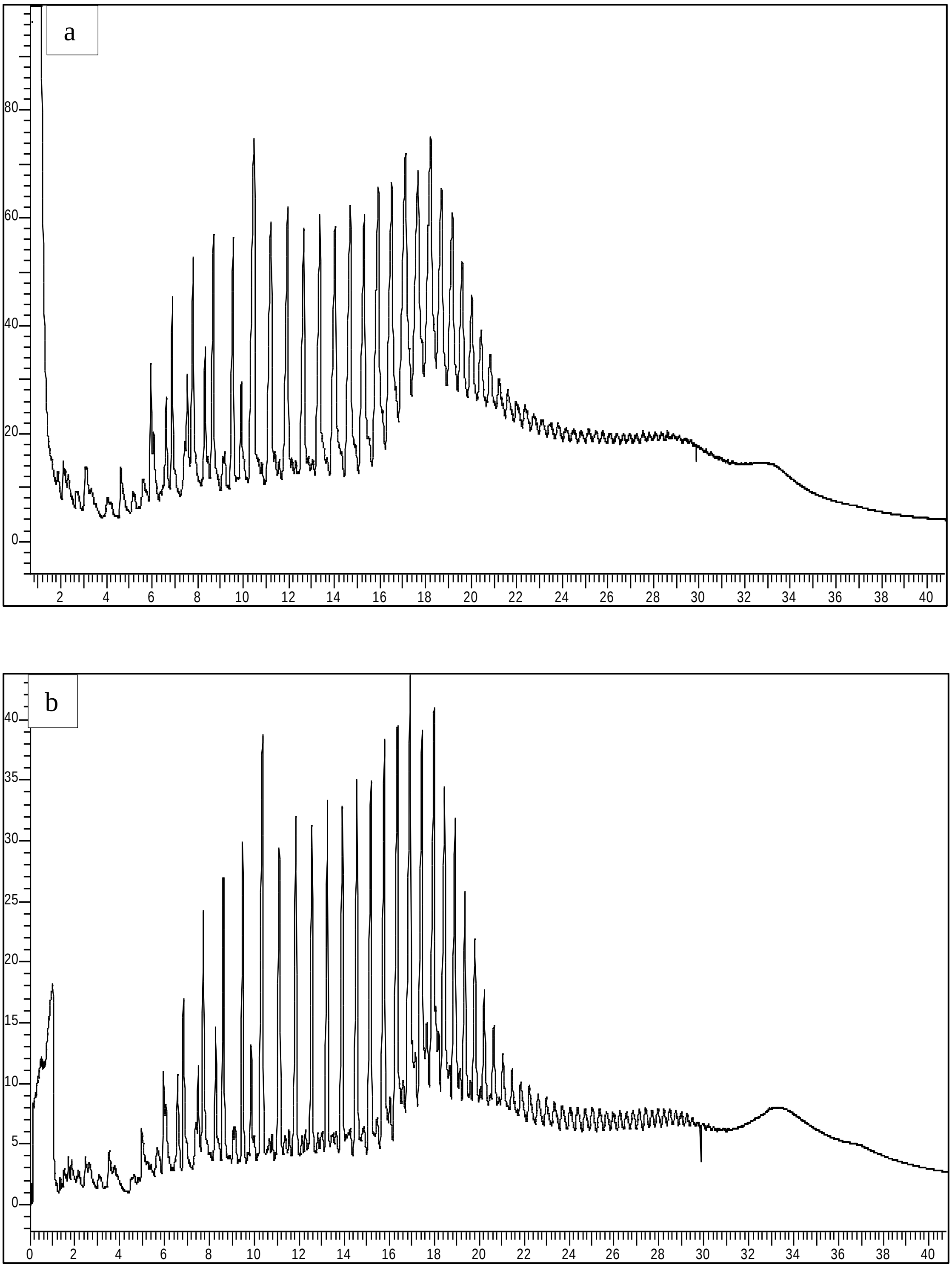


Figure A.4: Simdist Chromatogram of a) Crude A6, b) Crude A6 with PPD-A16

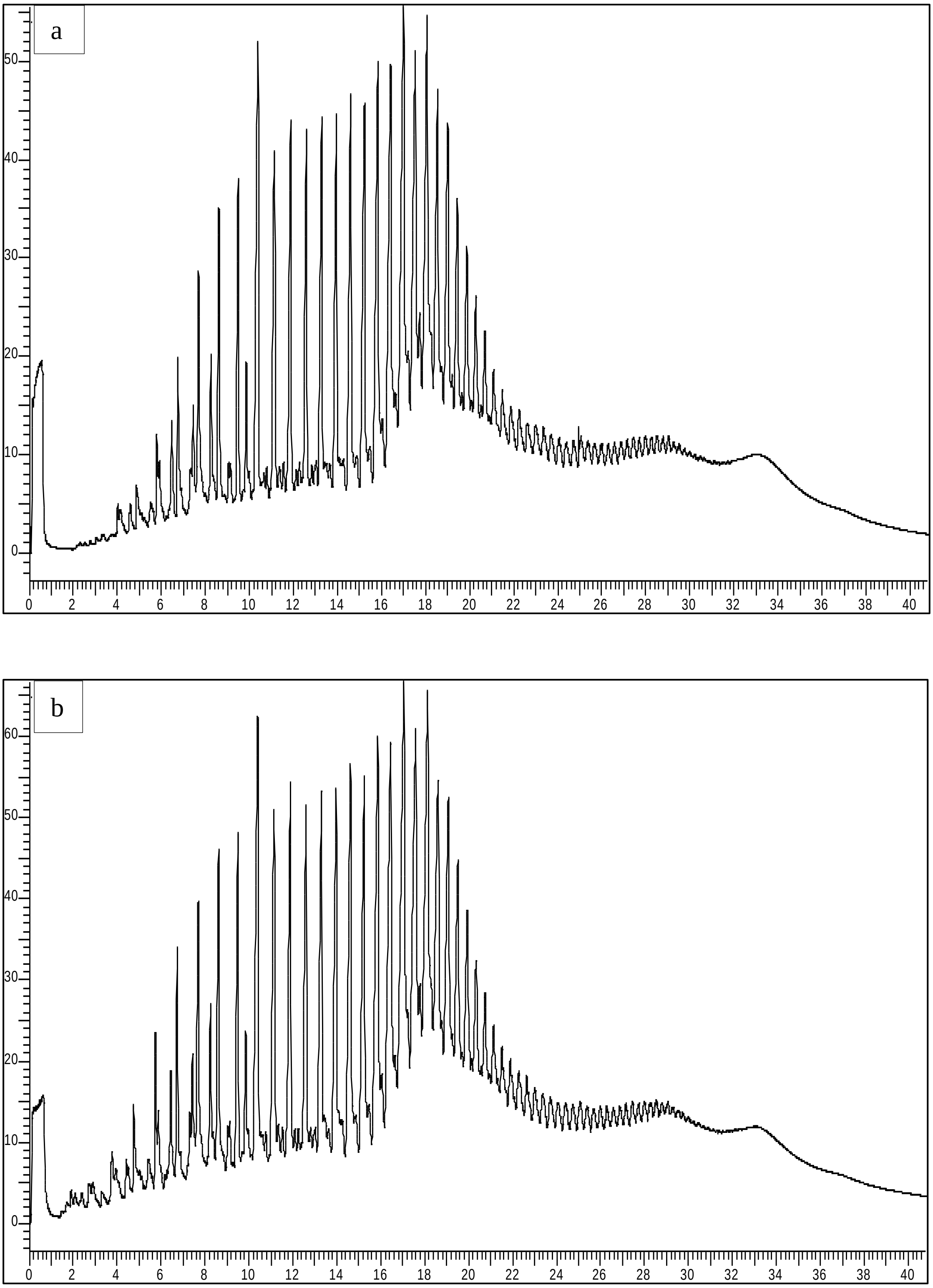


Figure A.5: Simdist Chromatogram of a) Wax A6, b) Wax A6 with PPD-A16

Table A.3: Boiling point of untreated and treated Crude A6 and Wax A6 with PPD-A16

	Unit	Untreated Crude	Treated Crude	% Reduction	Untreated Wax	Treated Wax	% Reduction
IBP	°C	143.5	137.5	4.18	172.5	150	13.04
5%	°C	213	215	-0.94	238	222.5	6.51
10%	°C	248.5	252.5	-1.61	273.5	260.5	4.75
20%	°C	311.5	310.5	0.32	328	317.5	3.20
30%	°C	367	365	0.54	378.5	370.5	2.11
40%	°C	410	407	0.73	415	410	1.20
50%	°C	437	431.5	1.26	439.5	435.5	0.91
60%	°C	463	456	1.51	465	460	1.08
70%	°C	499	493.5	1.10	502	495.5	1.29
80%	°C	547	544	0.55	554.5	547.5	1.26
90%	°C	598	597	0.17	606.5	603	0.58
95%	°C	622	621.5	0.08	630.5	628.5	0.32
FBP	°C	647	645	0.31	654.5	654.5	0.00