

CHAPTER III EXPERIMENTAL

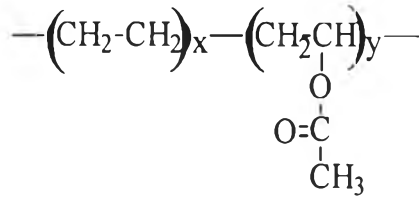
3.1 Chemical and Equipment

3.1.1 Chemicals:

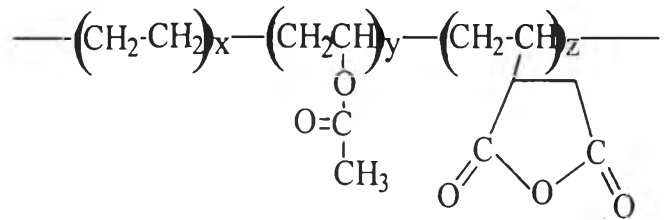
Three crude oil samples from different resources, Lankrabue-Kumphangphet (LK), U-thong-Suphanburi (UT), and Fang-Changmai fields (FA) were kindly supplied by Petroleum Authority of Thailand Exploration and Production, PTTEP (previously Thai-Shell Exploration and Production), PTTEP, and Defence Energy Department (DED), respectively. Poly(methyl methacrylate) or PMMA (VH and MD grades, 99.5% purity) was supplied by Siam Cement Co. Ltd. Poly(ethylene-co-vinyl acetate) (EVA) with vinyl acetate content of 18%, 25%, 33% and 40%, poly(ethylene-co-butyl acrylate-co-maleic anhydride) or PEBAMA (99.9% purity), poly(ethylene-co-vinyl acetate)-graft-maleic anhydride or EVAGMA (99.9% purity), poly(maleic anhydride-alt-1-octadecane or PMAO (99.9% purity) and poly(lauryl methacrylate-co-ethylene glycol or PLEGMA (99.9% purity) were obtained from Aldrich Company. Poly(octadecyl methacrylate or POMA (99.9% purity) was supplied by Carlo Erba. Three solvents (n-pentane, n-hexane, n-heptane, 99.5% purity) were obtained from Labscan Company. Chemical structures of some wax inhibitors are shown in Figure 3.1.

3.1.2 Equipment:

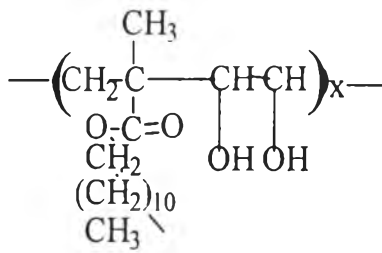
- Soxhlet extractor
- Test cells for pour point tester
- Thermometer (ASTM D86)
- Cooling jacket
- Simulated distillation gas chromatography (Sim-Dist GC), Varian GC-3800 model, Australia
- Differential scanning calorimeter (DSC), Perkin Elmer 2800, USA.



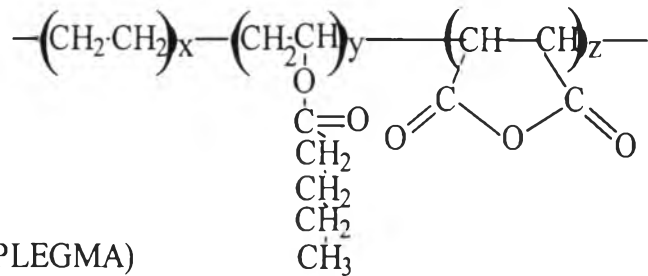
Poly(ethylene vinyl acetate) (EVA)



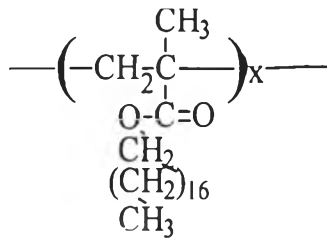
Poly(ethylene vinyl acetate)-graft maleic anhydride (EVAGMA)



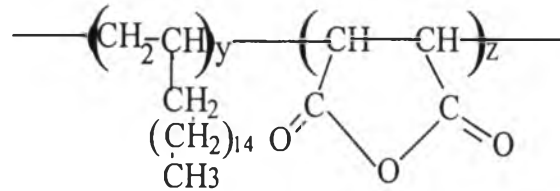
Poly(lauryl methacrylate)-co-ethylene glyco (PLEGMA)



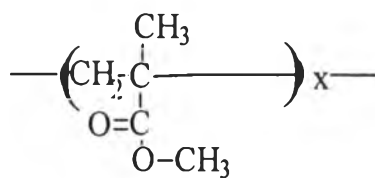
Poly(ethylene-co-butyl acrylate-co-maleic anhydride) (PEBAMA)



Poly(octadecyl methacrylate) (POMA)



Poly(maleic anhydride-alt-1-octadecane) (PMAO)



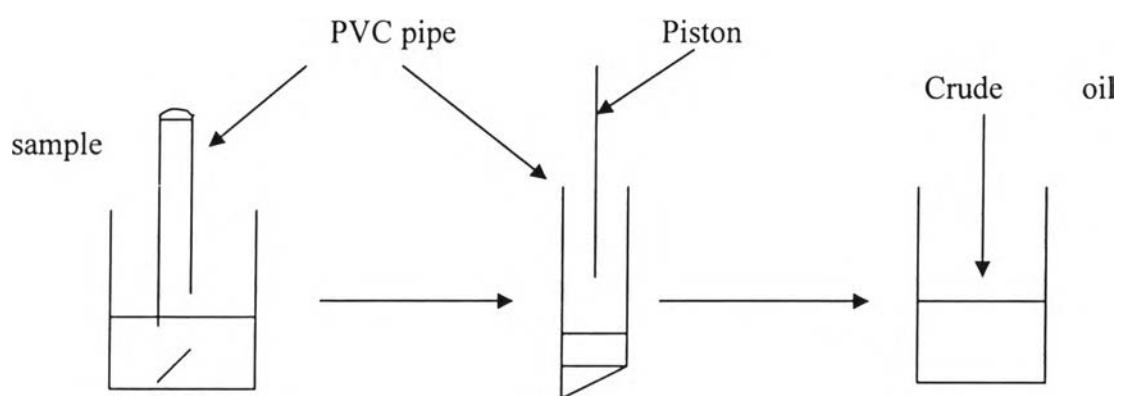
Poly(methyl methacrylate) (PMMA)

Figure 3.1 Structures of wax inhibitors. (Pedersen *et al.*, 2003)

3.2 Methodology

3.2.1 Sample Preparation:

Crude oil samples were semi-solid at room temperature. In order to avoid losing lighter components by heating, modified sampling tube using a PVC pipe (3 cm. diameter, 40 cm. long) was used as shown in Figure 3.1.



- a) Push down sampling tube into a crude sample in a gallon and then pull out
 b) Push out the crude oil inside the tube by a piston
 c) Collect crude oil in a container

Figure 3.2 Procedure of sampling preparation.

The sampling tube was pushed into the crude oil gallon until it reached the bottom then pulled out. The crude oil sample inside the tube was pushed out from the tube with a piston. The procedure was repeated at different locations across the surface of the crude oil in each gallon. All crude oil samples were collected in containers.

3.2.2 Characterization of Crude Oil

All tests for crude oil samples were characterized following ASTM standards.

3.2.2.1 Distillation

Distillation curves of crude oil samples were determined by using Stanhope-Seta distillation equipment following ASTM D86.

Heat is applied to the distillation flask and the contents and regulated so that the time from initial boiling to 5 or 10 % recovered is within 10 min. Then, the initial boiling point is observed and recorded. The heating is continuously regulated at the rate obtaining the distillate of 4-5 ml/min. The final boiling point is observed and recorded. Eventually the percent recovery and the temperature is reported.

3.2.2.2 Pour Point Testing

Both maximum and minimum pour points of crude oil were tested followed the ASTM D97 standard (Appendix C).

3.2.2.3 Determination of Wax Content

The wax content is determined by the modified UOP method 46-64 (Burger *et al.*, 1981) based on precipitation of wax in acetone (Appendix C).

3.2.2.4 Determination of Wax Appearance Temperature (WAT) and Wax Disappearance Temperature (WDT)

WAT during cooling (precipitation) and WDT during heating (dissolution) were measured using the differential scanning calorimeter (DSC, Perkin Elmer 2800, USA.). The DSC instrument was adjusted to both temperature and heat flow using pure indium as a standard reference. The heating and cooling rates were 5 °C/min. Detailed procedure is in Appendix C.

3.2.3 Crude Fractionation

3.2.3.1 Identification of Hydrocarbons Composition in Crude Oil

The hydrocarbons composition in the crude oil was determined by using simulated distillation gas chromatography (Sim-Dist GC, Varian GC-3800 model, Australia). The gas chromatograph was equipped with an on-column injector and a 10 m x 0.53 mm i.d., 0.88 µm CP7512 capillary column with flame ionization detector (FID). Helium carrier gas was at the flow rate of 60 ml/min and the column was programmed from 30 °C to 380 °C at the program rate of 10 °C/min. The crude

oil sample was heated to 80 °C and dissolved in carbon disulfide (CS₂) and the concentration of 0.01 g/ml was prepared. The solution was kept in a vial. One microliter of the sample was injected into the sim-dist GC using an autosampler.

3.2.3.2 Separation of Crude Oil

A novel and modified methods to fractionate the crude oil were studied and compared. A novel method (Nguyen *et al.*, 1999) separate the components in crude oil.

3.2.3.2.1 Nguyen's Method

One gram of oil (\pm 0.005 g) was dissolved in 10 ml of hot *p*-xylene (at least 80 °C) to ensure complete dissolution of any wax crystals. The asphaltene fraction was extracted by using a soxhlet extractor with *p*-xylene for 48 hr. This time period can be significantly reduced if the microcrystalline wax content ($>C_{40}$) is low. Then the *p*-xylene extract was concentrated to 5 ml. One hundred and ten cm³ of acetone was added to the concentrated solution and cooled to - 21 °C (Burger *et al.*, 1981). The precipitate (or wax) was filtered and dissolved in 30 ml n-pentane. The solution was cooled to - 21 °C and allowed to stand overnight. Finally two fractions were obtained, the macrocrystalline waxes in the solution and microcrystalline waxes as precipitate (a predominance of high molecular weight hydrocarbons). Both types of waxes were analyzed for hydrocarbons composition by sim-dist GC, and FTIR for asphaltene too

3.2.3.2.2 Modified Nguyen's Method

In previous work (Wison, 2004) was successfully modified to reduce separation time by replacing *p*-Xylene soxhlet extraction of asphaltene with n-heptane. As a reference, the solution was then cooled to 0 °C and left overnight. The asphaltenes as precipitate in the solution are removed by filtration. The following steps of wax precipitation and separation remain the same as Nguyen's method.

3.2.4 Effects of Inhibitors

The influence of wax inhibitors on the pour point and wax appearance temperature of Thai crude oils were studied by using 25 g of crude oil with varying concentration of wax inhibitors and solvents as shown in Table 3.1 and 3.2. Detailed

procedure is in Appendix D.

Table 3.1 Concentration of each wax inhibitor

Concentration (ppm, wt/wt)	100	200	400	600	800	1000
Weight (mg)	2.5	5	10	15	20	25

Table 3.2 Volume of each solvent

Volume of solvent (cm ³)	1.6	3.2	4.8	8	16	20	24	32	36	40
% wt/wt of solvent	3.8	7.4	10.7	16.7	28.6	33.3	37.5	44.4	47.4	50.0