1.0 Introduction

1.1 Research Background

Ethylene Vinyl Acetate (EVA) also popularly known as rubber or foam rubber used in biomedical and pharmaceuticals industry for example drug delivery service. The major problem that crude oil industry faced are high pour point, non-Newtonian flow behaviour wax deposition during the transportation of crude oil. These adverse properties resulting marked pressure drop during pipelining, reduced throughput and even pipeline blockage (Atta, 1997).

Ethylene vinyl acetate (EVA) is one of the leading materials in PPD industry. The ability to produce with high vinyl acetate (VA) content makes these techniques suitable to produce EVA and apply as pour point depressant.. The properties of Eva copolymer highly depend on the percentage of ethylene in copolymer (Choi and Kwang, 2009). The composition of EVA monomer is highly dependent for PPD application thus high efficiency EVA can be produced at extreme processing condition. EVA is polyolefin bearing polar vinyl acetate (VA) and it can be synthesized with various VA contents (Jeon, Ryu and Chang, 2003)

There are two key parameters that indicate the performance of EVA-type pour point depressants which are the weight percent of vinyl acetate in the copolymer and their respective melt index (MI). Polyethylene will undergo disruption as more vinyl acetate (VA) is added into the polymer. Hence, which will lower the melting point, modulus, and hardness of the VA. The addition of VA makes the polymer more polar, which improves adhesion to polar substrates and aids in solubility.

Nowadays emulsion is widely view as mass practical areas of interest due to their extensive in many application. Emulsion is a dispersion of two normally immiscible material that are stabilized by another material called as emulsifier. During agitation, the emulsion will form a suspension, a form where the water and oil will separate eventually in temporary time. Emulsion can be divided into two basic forms (Chern, 2005). The first one is oil-in-water (O/W) while the other one is water-in-oil (W/O). In crude oil industry, the stability of emulsion is very important. Stability means the capability of a formulation in a system to remain its originality throughout is shelf life. Stability testing will provide us:

- Evidence how to quality of emulsion system varies with times and temperature.
- Determine its shelf life.
- Determine recommended storage conditions of the emulsion system.

On the other hand, there a only a few studies on PPD emulsion thus, this emulsion technology are being less explored and exposed but it is beneficial to furthered studies since there are only a few people studies about it. PPD emulsion products are more advantageous for the use in sub-ambient temperature as it improves the physical handling characteristics compared to traditional products, Becker (1999). In the meantime, EVA copolymers are considered one of the best and the most stable materials in PPD application because of the efficiency of itself compared with other additives to treat crude oil.

Yet, there are no further studies to maintain or improve PPD emulsion stability in term of homogenization factors such as homogenization intensity, temperature and time. The most important is to maintain the stability of the emulsion product to ensure there are no separation occur during after temperature changes.

The concept of this project is to determine the performance of ethylene vinyl acetate (EVA) via emulsification process towards pour point depressant application.

1.2 **Problem Statement**

This techniques is suitable to produce EVA and apply as pour point depressant due to the ability to produce high vinyl acetate (VA) content. The properties of EVA copolymer highly depend on the percentage of ethylene in the copolymer (Choi and Kwang, 2009). High efficiency EVA can be produced at extreme processing conditions for its performance as PPD highly dependent on the composition of monomer inside. EVA is a polyolefin bearing polar vinyl acetate (VA) and it can be synthesized with various VA contents (Jeon, Ryu and Chang, 2003).

EVA production process commercially by the polymerization of emulsion. This polymerization happens when free radical diffuse into micelles and polymer partial formed via aqueous phase. Ethylene vinyl acetate (EVA) with high composition of vinyl acetate can be synthesized by using these techniques (Keung, 1974). Pour point depressant of EVA can also be produced by suspension polymerization. However, in this research, emulsion is preferred because when in suspension, high molecular weight of polymers cannot be formed. This is because, when high molecular weight is produced, the solvent molecules may act as chain terminators.

The presence of paraffin waxes in crude oil can interfere the flowability in pipeline transport by the increase the viscosity of the fluid and create precipitate on the wall that reduce the cross – sectional of the diameter of the pipeline. This incident can cause the blockage of valve that will increase the pressure and will cause also the increment of production cost. The formation of paraffin waxes occur because of lack of steric hindrance that should prevent the formation. In this case pour point depressants (PPD) that made from polymers will be use in order to prevent the formation of paraffin wax crystal link with others paraffin waxes.

There are many studies about PPD application with copolymer additives such as crystalline amorphous polymer, poly(methtl methacrylate) and comb polymers but there are less nanohybrids polymers used in this application. The main reason of the application of PPD in crude oil is to find the long term stability of the treated crude oil and may enhance of depletion processes in transport requirements.

There are many advantages using nanohybrids PPDSs, but the challenge is the crude oil production is under deep water thus the temperature is so cold and low. The wax appearance temperature (WAT) does not include at low temperature meaning at below zero Celsius. Cold flow might occur even the PPs have been out because the formation of wax paraffin crystal at low temperature. Thus, evaluation of performance nanohybrids PPDs will emphasize towards crude oil to find temperature where there is no flowing of the crude oil by using ASTM D97. So, we can study the flowability of the treated crude oil at low temperature as between 0 °C and the lowest is -20 °C can be carried out.

EVA production is commercially processed called emulsion polymerization. The mechanism of emulsion polymerization is when free radical is diffused into micelle and polymer particles are formed via aqueous phase. Ethylene Vinyl Acetate (EVA) with high composition of vinyl acetate can be synthesized by using this technique (Keung, 1974).

1.3 Research Objective

1.3.1 Effect of DEA:MWV ratio on rheological properties and shelf life study of emulsified EVA copolymer of PPD

1.3.2 Effect of sonication time on rheological properties and shelf life study of emulsified EVA copolymer of PPD

1.3.3 Performance of emulsified poly acrylate PPD

CHAPTER 2

LITERATURE REVIEW

2.1 Pour Point Depressant

2.1.1 Overview

Pour point depressant (PPD) is the solution to prevent formation of paraffin waxes and PPD is a chemical additive that contain homo and copolymers that used as inhibitor injection method. The mechanism of PPD in to inhibit paraffin waxes by reducing the size and the shape of crystals and co – crystallizes wax forming component of crude oil and limiting the degree of co- crystallization with polar components of the PPD. Some studies shows nanoparticle plays important roles in the heat distortion temperature, crystallization temperature and grain size of the nanocomposites. Nanoparticles polymers can increase the stability of nano- PPD and crystallization of n – alkenes long chains in paraffin wax. At low temperature, the viscoelastic behaviour of nano – PPD doped oil has weaker get network structure thus the paraffin wax with polymer additives stabilize the crude oil at liquid state rather than stable a solid state and affect the nucleation and crystallization of formation of paraffin wax.

Currently, there are two common ways to approach the problem caused by deposition of crude oil. Firstly is the temperature of crude oil must be maintain above its pour point temperature. However, this idea is not always technically or economically convenient. So, people start doing research and invent the new ways which is chemical pour point depressants so that it can modify the interaction the wax precipitate and will reduce the pour point and improve the flow characteristic. These compounds modify wax crystals habits, size and shape via nucleation, co crystallization and absorption and therefore improved wax solubility.

2.1.2 Mechanism of PPD

Crude oil production under deep water presents very serious operational problem. This is because due to possible obstruction of flow pipes or production lines. Those line always in contact with very cold sea water and the sharp decrease in temperature of oil production lines provokes the crystallization of some heavy oil fractions. The separation of those fractions, mainly by paraffin and waxes cause produces solid deposits responsible for the reduction of the flow lines cross – sections. Paraffin wax deposition from diesel fuel at low temperature is one of the serious and long-standing problems in the petroleum industry. At low temperatures, the crystals of wax easily form impermeable cakes, which can block filters and eventually lead to engine failure. Many methods have been attempted for the prevention of the crystals mating together. Since adding chemical additives (such as pour point depressants (PPDs), cold flow improvers, paraffin inhibitors or wax crystal modifiers) is the most convenient and economic way, it is widely used in the industry. It has been found that with the addition of the additives, the shape of the wax crystal changes. Many postulated mechanisms have been put forward to explain this phenomenon and to instruct the PPD product design. Among the mechanism theories, adsorption, co-crystallization, nucleation, and improved wax solubility are widely accepted by mechanism researchers.

2.2 Eva Copolymer

2.2.1 Overview

Ethylene vinyl acetate (EVA) is the combination of ethylene and vinyl acetate. The weight percent vinyl acetate usually varies from 10 to 40%, with the remainder being ethylene. EVA copolymer also can be referred as vinyl acetate modified polyethylene. EVA copolymer is copolymerized and processed as a thermoplastic film just like low density polyethylene. Thus the have the same properties but Eva copolymer has in increased gloss, softness and flexibility. Generally, EVA copolymer is known as non-toxic.

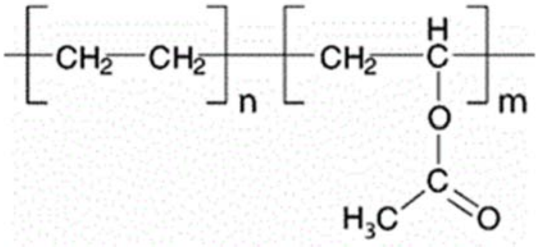

Figure 2.1: Molecular structure of ethylene vinyl acetate (EVA)

2.2.2 **Emulsified EVA copolymer as PPD**

Emulsion polymerization is on the polymerization technique that can be used ethylene vinyl acetate (EVA) into pour point depressant application. An emulsion polymerization system comprises water, an initiator (usually water soluble), a water-insoluble monomer and a colloidal stabilizer, which may be added or maybe formed in situ (Fanta, 1979). The techniques, process and mechanism (strategies mode of operation will influence the rate of polymerization and the characteristic of formed polymer. EVA act as PPD with

chemical structure resembles as comb polymer.

2.3 Emulsion

Emulsion is a mixture of two or more immiscible liquid for instance water and oil. Emulsion generally are part of class of two-phase system of matters that called as colloids. Emulsion can be divided into two basic forms (Chern, 2005). The first one is the oil-in-water (O/W) emulsion. In this emulsion, the oil droplets are dispersed and encapsulated within the water column. The second one is the water-in-oil (W/O) emulsion in which droplets of water are dispersed and encapsulated within the oil. In an emulsion, one of the liquid which is the dispersed phase dispersed in the other liquid called as the continuous phase. For example type of emulsion is homogenized milk, mayonnaise and some cutting fluid to cut metal.

2.3.1 Emulsion characteristic

- Initial Adhesive Strength High Wet Tack
- Good Creep Resistance
- Water Resistance
- Alkali Resistance
- Good Thickening Response
- Operation Safety

2.3.2 Emulsion stability

From thermodynamic point of view, the reason why an emulsion is unstable because there are natural tendency for a liquid system to separate and reduce the interfacial area between the two phases thus reduce the interfacial energy between those layer. Water in oil emulsion are considered to be special liquid in liquid colloidal dispersions. Their kinetic stability is because of the small droplet size and the present of and interfacial film around water droplets with the present of stabilizing agent also known as emulsifiers. These emulsifiers involved in the mechanism that would break down an emulsion. Such mechanism include:

- Aggregation or flocculation
- Coalescence
- Phase inversion
- Sedimentation

Sedimentation is the falling of water droplets from an emulsion because of the density difference between the oil and water. Aggregation or flocculation is the grouping together of water droplets in an emulsion without a change in surface area. Coalescence is the fusion of droplets to form larger drops with reduced total surface area. Oil demulsification discusses the mechanisms of emulsion breakup.

2.3.3 Factor affecting stability

Since interfacial films are primarily responsible for emulsion stability, it is important to understand factors that affect interfacial films. Important factors are:

- **Heavy polar fractions in the crude oil**

Naturally occurring emulsifiers are concentrated in the higher-boiling polar fraction of the crude oil. These include:

- Asphaltenes

  Asphaltenes are complex polyaromatic molecules defined to be soluble in benzene/ethyl acetate and insoluble in low-molecular-weight n-alkanes. They are dark brown to black friable solids with no definite melting point. Asphaltenes are considered to consist of condensed aromatic sheets with alkyl and alicyclic side chains and heteroatoms scattered throughout. The heteroatoms include:

  a. Nitrogen
  b. Oxygen
  c. Sulfur
  d. Trace metals like vanadium and nickel

  - Resins
  - Oil-soluble organic acids (e.g., naphthenic, carboxylic) and bases

- **Solids, including organic (asphaltenes, waxes) and inorganic (clays, scales, corrosion products, etc.) materials**

  These compounds are the main constituents of the interfacial films surrounding the water droplets that give emulsions their stability. Fine solid particles present in the crude oil are capable of effectively stabilizing emulsions. The effectiveness of these solids in stabilizing emulsions depends on factors such as:

  1) Solid particle size
  2) Interparticle interactions
  3) Wettability of the solids

  Solid particles stabilize emulsions by diffusing to the oil/water interface, where they form rigid films that can sterically inhibit the coalescence of emulsion droplets. Furthermore, solid particles at the interface may be electrically charged, which may also enhance the stability of the emulsion. Particles must be much smaller than the size of the emulsion droplets to act as emulsion stabilizers. Typically these solid particles are submicron to a few microns in diameter.

- **Temperature**

  Temperature can affect emulsion stability significantly. Temperature affects the physical properties of oil, water, interfacial films, and surfactant solubilities in the oil and water phases. These, in turn, affect the stability of the emulsion. Perhaps the most important effect of temperature is on the viscosity of emulsions because viscosity decreases with increasing temperatures. This decrease is mainly because of a decrease in the oil viscosity. When waxes are present (the temperature of the crude is below its cloud point) and are the source of emulsion problems, application of heat can eliminate the problem completely by redissolving the waxes into the crude oil. Temperature increases the thermal energy of the droplets and, therefore, increases the frequency of drop collisions. It also reduces the interfacial viscosity, which results in a faster film-drainage rate and faster drop coalescence.The effect of temperature on crude oil/water interfacial films was studied in some detail by [Jones et al] who showed that an increase in temperature led to a gradual destabilization of the crude oil/water interfacial films. However, even at higher temperatures, a kinetic barrier to drop coalescence still exists. Temperature influences the rate of build-up of interfacial films by changing the adsorption rate and characteristics of the interface. It also influences the film compressibility by changing the solubility of the crude oil surfactants in the bulk phase.

- **<u>Droplet size and droplet-size distribution</u>**

  Emulsion droplet sizes can range from less than a micron to more than 50 microns. Oil emulsions shows the typical droplet-size distributions for water-in-crude oil emulsion. Droplet-size distribution is normally represented by a histogram or by a distribution function.Emulsions that have smaller size droplets will generally be more stable. For water separation, drops must coalesce—and the smaller the drops, the greater the time to separate. The droplet-size distribution affects emulsion viscosity because it is higher when droplets are smaller. Emulsion viscosity is also higher when the droplet-size distribution is narrow (i.e., droplet size is fairly constant).

- **<u>pH of the brine; and brine composition</u>**

  The pH of water has a strong influence on emulsion stability.[2][3][4] The stabilizing, rigid emulsion film contains:

  - Organic acids and bases
  - Asphaltenes with ionizable groups
  - Solids

  Adding inorganic acids and bases strongly influences their ionization in the interfacial films and radically changes the physical properties of the films. The pH of water affects the rigidity of the interfacial films. It was reported that interfacial films formed by asphaltenes are strongest in acids (low pH) and become progressively weaker as the pH is increased. In alkaline medium, the films become very weak or are converted to mobile films. The films formed by resins are strongest in base and weakest in acid medium. Solids in the emulsions can be made oil-wet by asphaltenes, an effect that is stronger in an acidic than in a basic medium. These partially oil-wet solids tend to stabilize water-in-oil emulsions.

2.4 Role of surfactant in emulsion

2.4.1 Overview

The primary role of surfactants in emulsion polymerization is to lower the interfacial tension between water and oil which will allow the emulsification of vinyl polymer which is EVA in this project and the formation of stable colloidal dispersion of nano-size polymer particles. There are 3 types of surfactants which is ionic, cationic and non-ionic. In this case Tall oil fatty acids (TOFA) also known as MWV and Diethanolamine (DEA) acts as non-ionic surfactants.

2.4.2 Tall Oil Fatty Acids (TOFA)

Tall oil fatty acids also known as liquid rosin is a viscous black-yellow solution and also odourless obtained as side product of the Kraft process of a wood pulp manufacture when pulping mainly coniferous trees. Kraft process is a process for converting wood into wood pulp which consists of almost 100% pure cellulose fiber, the main component for paper making. The component of crude tall oil depends on the wood used. This tall oil fatty acids mainly use as adhesives, rubber and ink. In this case. Tall oil fatty acids acts as emulsifier for the emulsion. Emulsifier acts as sort of adhesives for water and oil solution because it will keep the droplets inside the emulsion well dispersed. An emulsifier consists of water – loving hydrophilic head and oil – loving hydrophobic head. The emulsifier will position itself in the between of water and oil interface by reducing the surface tension and has s stabilizing effect of the emulsion.

2.4.3 Diethanolamine (DEA)

Diethanolamine (DEA) in an organic compound with the formula of $HN(CH_2CH_2OH)_2$. In room temperature, DEA is white solid and has a tendency to absorb water and to supercool so DEA often encountered as colourless and viscous liquid. DEA is polyfunctional which being secondary amine and a diol. DEAa is used as surfactants and a corrosion inhibitor. In this case, we mostly discuss on DEA as surfactants.

2.5 Emulsification

2.5.1 Normal mixing method

Polymer intercalation has been proved as a successful approach to synthesize nanophase organic – inorganic hybrids. For instance, mica type silicates. There are three types of polymer intercalation which are in-situ polymerization intercalation, solution intercalation and melt intercalation. Solution intercalation is chose because mostly in this project liquid state materials will be used. Solution intercalation is a process where based on a solvent system in which the polymer is soluble and the filer are swellable (Greenland DG 1963). The layered filler are swollen first in a solvent such as toluene, water and chloroform. When the polymer and filler are mixed, the polymer chain intercalates and will remove the solvent within the interlayer of the filler.

2.5.2 Sonication

Sonication is a process in which sound waves are used to agitate particles in solution. Such disruptions can be used to mix solutions, speed the dissolution of a solid into a liquid (like sugar into water), and remove dissolved gas from liquids. Sound is a wave made up of alternating regions of high and low pressure. Imagine yourself as a particle. As a sound wave passes you, you experience moments of high pressure (like at the bottom of a hill of a roller coaster when you feel pressed into your seat) separated by periods of low pressure (like at the top of a hill of a roller coaster when you feel 'weightless'). The frequency of a sound wave is a measure of how often the particles of a substance vibrate (how quickly you transition from the 'top' feeling to the 'bottom' feeling of a roller coaster). The sound waves used in sonication are usually ultrasound waves with frequencies above what you can hear (above 20 kHz that is 20,000 cycles per second) and as frequency increases the strength of the agitation increases. In solution, the particles vibrate because as they experience cycles of pressure, microscopic vacuum bubbles form and then collapse into solution, a process called cavitation. These vibrations can disrupt molecular interactions (e.g. between molecules of water), break clumps of particles apart, and lead to mixing. In the case of dissolved gas, these vibrations can allow the gas bubbles to come together and more easily leave the solution.

2.6 Shelf life of emulsion

2.6.1 Aging at room temperature

The emulsions were kept in glass bottles at room temperature (approximately 34°C) to simulate bulk storage environment. The characterization was done by progression of weeks in order to observe the effect of storage period on droplet size. Similarly in this experiment, any unstable emulsions were ruled out as samples with visible oil phase presence in the bottles.

2.6.2 Freeze thaw test

The samples of emulsion were weighed and transferred into glass bottles to simulate bulk storage environment during the freeze-thaw cycle. The emulsions were held for 22 h at temperature beyond -10°C before thawing to 50°C for another 2 h. This cycle was repeated every weekdays and the characterization was done by 10 progression of weeks. Any unstable emulsions were ruled out as samples with visible oil phase after the freeze-thaw cycle.

2.7 Pour point test based on ASTM D-97

Pour point is defined as the highest temperature at which the fuel loses its flow characteristics. The test will be conducted according to ASTM D97 with the setup as shown in Figure 3.2; the sample is cooled at a specified rate and examined at intervals of 1°C for flow characteristics. The lowest temperature at which movement of the specimen is observed is recorded as the pour point. In order to determine the pour point reduction performance of the performance, the differences between the pour point of treated and untreated wax solution will be measured (Machado et al., 2001), using the formula;

$$\Delta PP = PP_{before} - PP_{after} \qquad \text{Equation 2.1}$$

ΔPP = Pour Point Reduction

PP_{before} = Pour Point of untreated wax solution

PP_{after} = Pour Point of treated wax solution

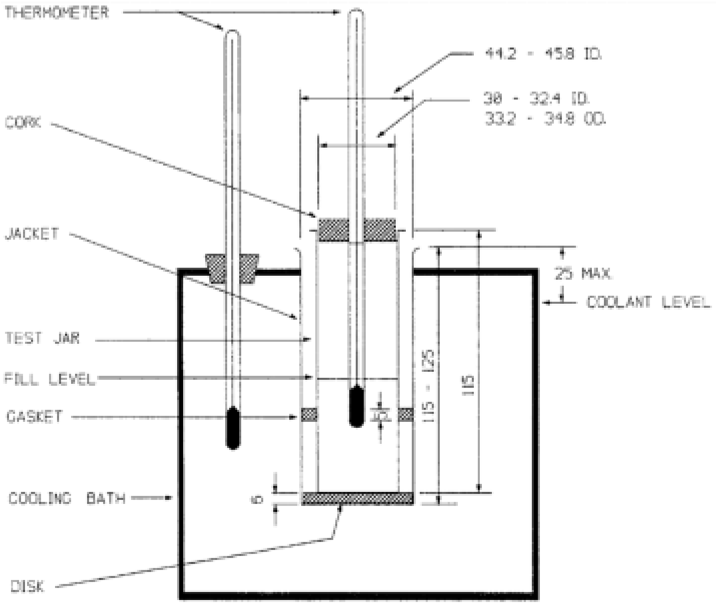

Figure 2.1: Pour point test setup as described in AST

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Materials

1) EVA copolymer
2) Xylene
3) Ethylene glycol
4) Diethanol amine
5) Tall fatty acid
6) Span 80
7) The solvents including benzene, acetonitrile, methanol, ethanol and water
8) Sulphuric acid (>96%)
9) Potassium permanganate (≥99%)
10) Calcium hydride (95%)
11) 1, 4-dioxane (99.8%),
12) N, N-dimethylformamide (DMF)

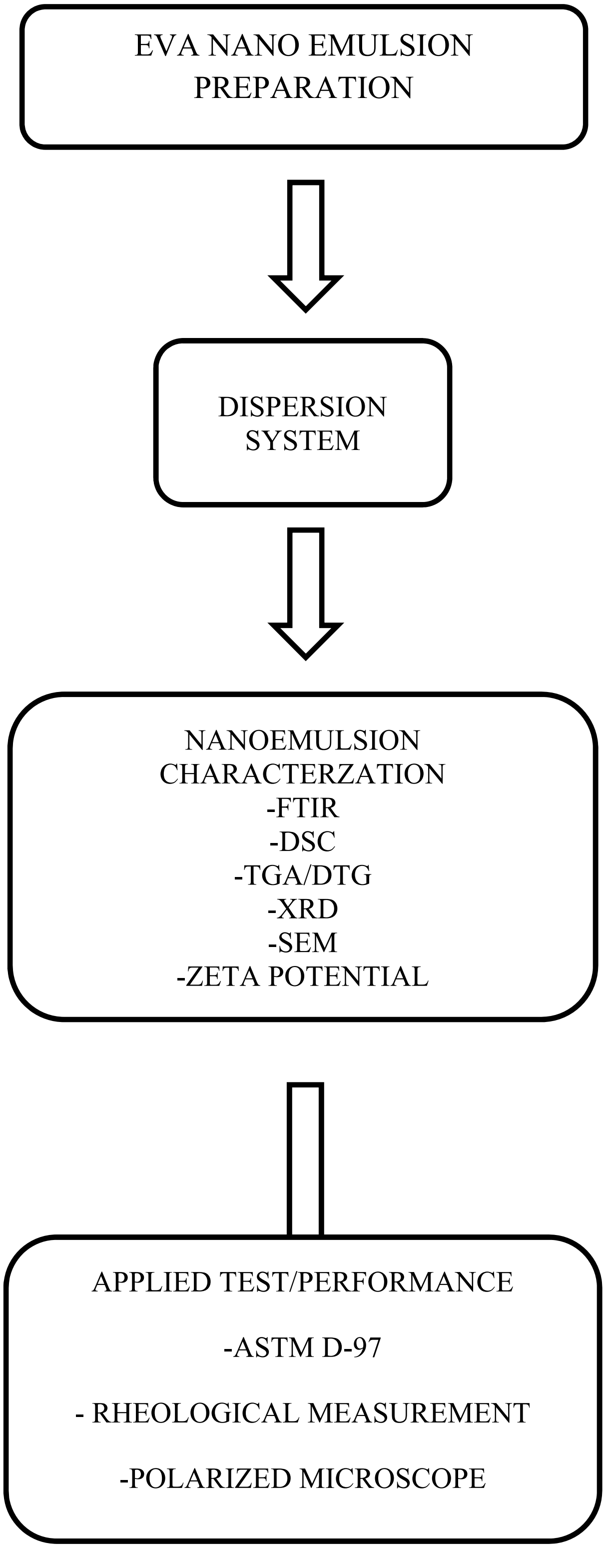

Figure 1.1: Overall experimental design flowchart of EVA-Graphene nanoemulsion composite process

3.2 Preparation of EVA Emulsion

Dissolution method

Emulsions were prepared by first dissolving the EVA pellets in xylenes using slow melt dissolution technique for approximately 30 minutes or until the pellets dissolved completely in the solvent. This procedure was done using triple-blade stirrer at particularly low speed and low temperature – about 300 rpm at 60°C, in order to avoid air bubble trapped inside the solution. The melt solution was later mixed with pre-dissolved surfactant solution, water containing DEA and mixture of distilled water – antifreeze according to formulation given in

Table . The mixing was done using the same equipment but at higher speed of 500 rpm at 50°C. Then, repeat the experiment using different loading of TOFA and DEA according the formulation given in table 1.2.

Table 3.1: The overall components in EVA emulsion used for PPDs application

Phase	Material	%
Oil phase	*EVA pellets*[a] *Xylenes*	*35*
Continuous phase[b]	*Distilled water* *Antifreeze (EG, PG, Glycerol)*	*60*
Surfactant	*Tall oil fatty acids (TOFA)*	*4*
Viscosifier	*DEA*	*1*

[a] EVA pellets content is 15 wt.% of the total oil phase

[b] The ratio of antifreeze-water mixture is 1:1

Formulation/Sample (g)	D0	D25	D50	D75	D100
Ethylene Vinyl Acetate (EVA)	35	35	35	35	35
Xylene					
Water	60	60	60	60	60
Ethylene Glycol (EG)					
Tall Oil Fatty Acid	4	3.75	2.5	1.25	0