SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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PREPARATION OF ACRYLATE BASE GRAPHENE AND GRAPHENE OXIDE (GO) NANOCOMPOSITE VIA PHYSICAL BLENDING AS POUR POINT DEPRESSANTS (PPD)

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation **"Preparation of Acrylate Base Graphene and Graphene Oxide Nanocomposite via Physical Blending as Pour Point Depressants (PPD)"**. I also declared that it has not been previously submitted for the award for any degree or diploma or other similar title of this for any other examining body or university.

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Witness by

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Date : 22 July 2017

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LIST OF SYMBOLS

°C	Degree Celcius
g	Gram
µm	Micrometer
%	Percentage

LIST OF ABBREVIATIONS

PPD	Pour Point Depressants
NPPD	Nano-hybrid Pour Point Depressants
WAT	Wax Appearance Temperature
DSC	Diffrential Scanning Calorimetry
DEA	Diethylamine
POM	Polarized Optical Microscope
JAYPOL 658G	Acrylate Polymer
EJN	Emulsified Jaypol Normal
EJG	Emulsified Jaypol Graphene
EJGO	Emulsified Jaypol Graphene Oxide
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermogravimetric Analysis
MWV	Meadwestvaco
G	Graphene
GO	Graphene Oxide
XRD	X-Ray Diffraction Spectroscopy
SEM	Scanning Electron Microscopy
PAAm	Pickering emulsions of aqueous acrylamide

PENYEDIAAN ASAS AKRILAT GRAPHENE DAN GRAPHENE OKSIDA JENIS NANOKOMPOSIT MELALUI PROSES PENGADUNAN FIZIKAL SEBAGAI AGEN TEKAN TITIK TUANG (PPD).

ABSTRAK

Bahan bersaiz nano seperti Graphene dan Graphene Oksida boleh diaplikasikan sebagai bahan percampuran didalam PPD beremulsi sejak ianya boleh menambah baik ciri-ciri PPD. Melalui penggunaan cara larutan interkalasi sebagai proses pengadunan fizikal, ianyatelah digunakan untuk memastikan Graphene dan Graphene Oksida berterabur dengan baik dalam PPD emulsi. Graphene telah dilarutkan di dalam air suling, kemudian campuran tersebut akan di kacau menggunakan mesin mekanikal selama 30 minit. Manakala Graphene Oksida dimasukkan kedalam air suling, etilina glikol dan MWV, kemudian campuran tersebut di kacau selama dua minit. Selepas itu, bahan kimia yang berasaskan minyak dan asas akrilat telah di masukkan ke dalam campuran bahan asas air, kemudian di kacau selama satu jam. Pada penyediaan sampel yang terakhir, campuran tersebut telah di kacau menggunakan mesin mekanikal selama tiga minit untuk mendapatkan penyebaran yang baik antara zarah nano saiz dengan PPD beremulsi. Dengan itu, penyebaran yang baik akan menghasilkan interaksi ‘van der wall’ di antara zarah nano size dengan asas akrilat. Beberapa ujian telah dilakukan untuk mencirikan sampel yang telah siap. Antara ujian yang dilaksanakan ialah Fourier Transform Infra-Red (FTIR), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM), Thermogravimetric analysis (TGA), X-Ray Diffraction (XRD), Penyebaran saiz zarah, potensi zeta, ujian aging , ujian beku cair, ASTM D97. Untuk keputusan ujian FTIR, kumpulan hidroksil telah dikenal pasti wujud dalam PPD sampel beremulsi dengan kehadiran air suling dan etilena glikol. Manakala kumpulan ester dan kumpulan karboksilik menunjukkan petanda kehadiran bahan zarah nano saiz dalam emulsi. Untuk DSC termogram, ianya boleh memudahkan kesemua Nano-hybrid PPD berimulsi mempunyai penyaliran yang baik dalam persekitaran yang sejuk atau pada suhu yang rendah jika dibandingkan dengan Normal PPD beremulsi (tanpa zarah nano saiz). Dalam TGA, ke semua Nano-hybrid PPD beremulsi terurai sepenuhnya pada suhu 480°C. Berdasarkan kepada keputusan ujian XRD, Nano-hybrid PPD beremulsi menunjukkan penghabluran yang tertinggi jika dibandingkan dengan Normal PPD beremulsi. Pengukuran saiz zarah membuktikan, semakin bertambah bilangan kitaran minggu untuk ujian beku cair dan aging, penyebaran saiz zarah dan potensi zeta berubah, hal ini kerana penyebaran saiz zarah tidak stabil apabila zarah nano saiz dimasukkan kedalam PPD beremulsi. Untuk ujian tekan titik buang (ASTM D97), Nan-hybrid PPD beremulsi yang mempunyai 1500ppm dos PPD beremulsi menunjukkan kecekapan yang baik untuk mencurahkan prestasi titik sebagai peningkatan aliran. Hal ini kerana, penurunan suhu ujian tekan titik tuang menunjukkan yang paling terbaik.

PREPARATION OF ACRYLATE BASE GRAPHENE AND GRAPHENE OXIDE (GO) NANOCOMPOSITE VIA PHYSICAL BLENDING AS POUR POINT DISPERSSANT (PPD).

ABSRACT

The nanoparticle material such as Graphene and Graphene Oxide can be applied as an additive in Emulsified Pour Point Depressant since it can be improvise the properties of PPD. By using solution intercalation method as physical blending to produce Graphene and Graphene Oxide well disperse in Emulsified Pour Point Depressant. Graphene dissolved in water, and then the mixture has been sonicate for 30 minutes. While, Graphene Oxide was pour in water, ethylene glycol and MWV, and then stir for two minutes. After that, the oil basecontaining acrylate polymer was pour into water base mixture, then it stirred for 1 hour. Finally, the mixture was sonicate in preparation sample around 3 minutes to get better dispersion between nanoparticles with emulsified PPD. Thus, the good dispersion are held together by the Van der Waals interaction between nanoparticles with acrylate polymer. Fourier Transform Infra-Red (FTIR), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM), Thermogravimetric analysis (TGA), X-Ray Diffraction (XRD), Particle Size Distribution, Zeta Potential, Aging Test, Freeze Thaw Test, ASTM D97 were conduct to characterize the sample.Using FTIR result, hydroxyl group was identified in the emulsion sample that justified with the presence of water and ethylene glycol. In addition, the ester group, carboxylic group and hydroxyl group shows the presence of nanoparticles material in emulsion. It can be simplified for DSC thermogram, all Emulsified Nano-hybrid PPD had better cold flow properties compared to Normal Emulsified PPD (without nanoparticles). In TGA, all Emulsified Nano-hybrid PPD decomposed completely at 480°C. Based on XRD results, Emulsified Nano-hybrid PPD

shows the highest crystallinity compared to Normal Emulsified PPD. The particle size measurement proved that, cycle per week for aging increased and freeze thaw test also increase the particle size distribution and zeta potential changes, since the colloidal of particles are not in stable when nanoparticles doped in emulsion. Furthermore, using the pour point reduction test, Emulsified Nano-hybrid PPD with optimum dosing (1500ppm) is the most effective sample act as PPD since it show the most pour point reduction containing 16°C compared to other samples.

CHAPTER 1

INTRODUCTION

1.1 Research background

Special alternative way have been given to the wax solidification in the oil and gas production industry. The precipitation of wax crystal from crude oil can cause significant issues during production, transportation and storage. The solidification of paraffin wax will form solid deposits, which reduce the cross-section of flow lines (del Carmen Garcia 2001). The precipitation of paraffin can occur for a variety of reasons and while the paraffin content and composition of the crude are important, typically temperature or pressure changes are the main offenders.

Several methods have been develop to minimise the problems caused by wax crystals deposition and aggregation. The prevention technique is mechanical remediation (pigging), applying heat or using hot solvent flush and the chemical inhibitor treatment such as poly(acrylate) base as pour point depressants (PPD), thermodynamic wax inhibitor (TWI) and crystal modifiers (Yang et.al(2015). Nevertheless, the chemical prevention of wax precipitation is preferred. Chemical treatment is chosen to inhibit of wax deposition since chemical treatment is more economical and more efficient compared to other methods.

Generally, pour point depressants selected in treating the wax deposition via chemical inhibitor treatment. Manka et.al (1999) found that, pour point depressants (PPD) are polymeric materials with long hydrocarbon chains that interact with the paraffin in the crude and inhibit the formation of large wax crystal matrices. The interaction retards the wax crystal formation and growth, alters the paraffin's heat of crystallization and depresses the crude's pour point while affecting the size and shape of the wax crystals. According to Yang et.al (2015), most polymeric additives is categories as crystalline-amorphous copolymers, ethylene-vinyl acetate copolymers and comb polymers. Hence, pour point depressants consists of polymers, which has comb structure that avoid the wax crystal growth on pipeline wall.

Acrylate polymer such as ethylene vinyl acetate (EVA) and poly methacrylate (PMA) become preferred choice in treating wax deposition. It is because EVA is a block olefin copolymer with rubber like properties and has excellent viscosity modifier properties (Totten, 2003). Meanwhile, PMA is known as comb polymer family due to their comb-like structure. Comb polymer has excellent ability to act as pour point depressant since it can withstand low temperature condition, which is below 0°C (Totten, 2003).

Mostly conventional polymeric PPDs are in solution form. This limits the PPD application in at cold climates for example during winter season. This is because PPD solutions are easily solidified at low temperature. The solidification problem of PPD will ruin the treatment itself as it cannot be injected into the pipeline in solid form (Becker, 1999). The costing for preheating and dilution is a prerequisite to be considered for its utilization in a crude oil industry. So, it is impractical to use the PPD solution in the cold environments.

Emulsion technology has been viewed to solve the PPD solidification at room temperature. According to Admiral et.al (2016), they successfully established the emulsion PPD which could flow at room temperature. At the same time, the behaviour of emulsion such as freezing point, viscosity at room temperature, particle size and zeta potential still improved. Nevertheless, there is some issue on PPD performance at emulsion even it possesses a good thermal stability emulsion. Introduction of Nano-size filler into a polymer become a well-known method to enhance the existing polymer properties (Boccaccini et.al, 2010). This polymer classification is known as polymer nanocomposites. This polymer nanocomposites concept can be employed to boost the PPD emulsion in treating the paraffin wax.

In recent year, graphene and graphene oxide become the current attention in research world. It gives positive impact toward the polymer Nano composites properties. Graphene is the strongest material because of π–π stacking in chemical structure. The π–π bond is described as the non-covalent interactions, which involves in the stacking of aromatic molecules. Aromatic network of sp^2 carbon atoms makes this interaction important in graphene functionalisation.

Graphene and graphene oxide were applied in biomedical field. Graphene was used as a substrate for addition or adsorption of molecules and the functional groups in a controlled manner (Mao et.al, (2013). Covalent and noncovalent surface modifications have been performed to improve biocompatibility and colloidal stability.

In this work, graphene and graphene oxide was used to study the behaviour of nanocomposite in the PPD emulsion and improve the PPD performance. In addition, the research work on graphene and graphene oxide in PPD application still limited. So, it is importance to gain a new generation of Nano hybrid pour point depressants used in oil and gas technology application.

1.2 Problem Statement

The conventional PPD faced with the solidification issue, since at room temperature, it will solidify. In addition, it is difficult to deliver the high active content of polymer at low viscosity value. According to (Becker, 1999), some PPD is less efficient especially for pour point reduction. If PPD dissolve, it is quite hard to achieve high active content, hence higher dosage of PPD must be used. The implication is that high dosage contributes to high treatment cost. The conventional PPD consists of active content in the range of 5-10 wt. %.

According to (Admiral, Abdullah et al. 2016) suggested the emulsion method on PPD to solve the solidification issue. However, it still has limitations on PPD performance. It is ideal to get a PPD which can be utilized any kind of temperature. The advantage for proposing nano hybrid pour point depressant are the active content in range 30-50wt% can be achieved and high molecular weight and environmental friendly (reduce solvent usage) PPD can be produced. However, PPD emulsion still lacks in term of application performance even possess a good flow-ability at low temperature. Since the performance of PPD is merely dependable on the existing of polymer properties.

The performance issue can be solved by incorporating of graphene and graphene oxide with Emumlsified PPD. It is interesting alternative when graphene can boost the PPD performance. Addition of graphene and graphene oxide in the PPD emulsion is very promising route to solve the above problem as it can produce an immense improvement in polymer properties. Graphene consists of π-π interaction which is noncovalent interaction involve in the stacking of aromatic ring molecules. This interaction prevents graphene aggregation through steric or electrostatic repulsion. Therefore, in this study, it is hypothesized that the graphene and graphene oxide will improve the PPD performance through steric or electrostatic repulsion. This repulsion force will prevent the crystal growth formation on the pipeline wall. In addition, Nano hybrid PPD is predicted to produce high total solid content (TSC) around 30-50 wt. % with low viscosity for emulsion compared to the PPD solution.

The suitable method to achieve the dispersion of nanocomposite in emulsion is the solution intercalation method. Solution intercalation is the method based on solvent system in which polymer is soluble and the silicate layers are swellable. When polymer and layered silicate are mixed, the polymer chain intercalate and displace the solvent within the interlayer of the silicate. Solvent removal, the intercalated structure remained. It helps the graphene dispersion.

Solution intercalation method was chosen, because it helps the incorporation of graphene and graphene oxide dispersion. The dispersion of graphene in solvents is most commonly achieved by sonication, which creates shear stresses and cavitation in the solvent. This has the effect of breaking apart graphite and exfoliating the sheets into individual graphene flakes. Shi et.al, (2007) proved that, the nanocomposites have an intercalated-and-flocculated structure. Nanocomposite material shows the enlarged d-spacing values indicate the intercalation of alkyl ammonium within silicate layers.

The integration of graphene and graphene oxide in the PPD emulsion give a new alternative for the manufacturer petroleum industry to improve their performance of current PPD product. Moreover, graphene and graphene oxide more economical that it can reduced the costing.

1.3 Objectives

1. To prepare poly (acrylate) emulsion filled with graphene and graphene oxide via solution intercalation method.

2. To achieve better performance of the Nano-emulsion PPD based on their characterization data.

3. To evaluate the statistical relationship between Nano-particle loading and PPD performance status.

1.4 Thesis Structure

In this thesis, there are five chapters discusses on poly (acrylate) base of graphene and graphene oxide as Nano-hybrid pour point depressants. A brief description on each chapter are elaborated as follows:

- **Chapter 1** briefly introduced the research project. This chapter covers the introduction about the research background, problem statement, objectives and outline of the thesis.

- **Chapter 2** is the literature review part. In this chapter, it covers brief introduction on graphene and graphene oxide. This chapter also covers the overview of background pour point depressants, development of pour point depressants, mechanism of pour point depressants, and general intro of PPD -

emulsion. Application of Nano-hybrid polymeric material in advancement of polymer nanocomposites and graphene in polymeric pour point depressant and emulsion product discussed. Moreover, several physical blending method has been review in this chapter such as in situ intercalative polymerization, solution intercalation and melt intercalation method. The best method has been chosen to be applied in physical blending of graphene and graphene oxide in emulsified PPDs.

- **Chapter 3** covers the methodology used in this works including materials, experimental method that is physical blending process, sample characterization, applied test and evaluation of emulsion.

- **Chapter 4** consists of results and discussion of the research project

    - **4.1** focuses on the results characterization of different system (Normal/Graphene/Graphene Oxide). The testing conducted including Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR), Thermal Gravity Analysis (TGA), Polarize Optical Microscopy (POM), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Particle Size and Zeta Potential.

    - **4.2** focuses on the results characterization of Graphene Oxide loading. The testing was conducted such as Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR), Thermal Gravity Analysis (TGA), Polarize Optical Microscopy (POM), X-Ray

  Diffraction (XRD), Scanning Electron Microscopy (SEM) and Particle Size and Zeta Potential.

  - **4.3** focuses on application of Nano-hybrid pour point depressants. In the application of Nano-hybrid PPDs section, Pour Point Measurement Based on ASTM D97, Impact of Nano-hybrid PPD on Zeta, Effect of Different Dosage and Impact of microstructure of paraffin wax (POM) are discussed.

- **Chapter 5** concludes the findings from the research project with few recommendations for future work.

CHAPTER 2

2.1 Pour Point Depressants

2.1.1 Overview Background of PPD

Dispersants are often blended with polymeric inhibitors to improve the additive performance. Low cost wax dispersants include alkyl sulfonates, fatty amine ethoxylates and other alkoxylated products. These products function well only when blended with polymeric inhibitors, (Hassan Ali, 2012). Normal method to controlling wax deposition for subsea pipelines is by regular pigging. According to Figure 2.1, this method improved the flow due to the passing pig is probably caused by a combination of smoothing of the rough wax layer and removal of the wax back into the flowing oil. The smoothing of the pipeline deposits can significantly reduce the friction factor in turbulent flow (Bern, Withers et al. 1980).

Figure 2.1: Wax deposition (left) and gelation (right) of waxy crudes in pipeline (F.Yang et.al, 2015).

According to Chen et.al (2010), they have found, the treated PPD will change the structure of paraffin mixtures is partially transformed from orthorhombic into hexagonal form. This is important in wax plays the role of lowering the melting point of wax.

Polymeric material has been develop to modify the flow properties of lubricants so that they can function adequately through a wide temperature range. Prior to the 1930s, several method that they used such as heats the solution, addition of kerosene to the lubricant and lastly they used asphaltenic resins for removing the wax crystal growth. It is due to the materials can be depress the pour point of oil. The first materials polymeric pour point depressants have been designed such as, poly alkyl methacrylate (PAMAs), again based on waxy alkyl group. Over the years, a wide variety of synthetic materials has been introduced commercially as pour point dispersant, however polymeric PPDs remain the most commercially viable option and include but are not limited to acrylates, alkylated styrene's, alpha olefins, ethylene /vinyl acetates, methacrylate's, olefin/maleic anhydrides (Hochheiser,1986).

Polymeric materials have been advanced adequately to function for a wide temperature range by modify the flow properties of lubricants. There are few types of polymer commonly used, as wax prevention chemical, which are, is olefin-based polymer and ester polymer. Ethylene vinyl acetate (EVA) and poly methacrylate (PMA) are the most common types of olefin and ester polymer used nowadays. Both types of the polymer has their own advantages and disadvantages. EVA is a block olefin copolymer with rubber like properties and has excellent viscosity modifier properties (Totten, 2003). However, it has lower pour point ability compare to PMA. Pour point is the lowest temperature which fuel or oil will pour under low temperature condition while pour point depressant (PPD) is the chemical used to enhance the pour point of the fuel. PMA is belongs to acrylate family or commonly known as comb polymer family due to their comb-like structure. Comb polymer has excellent ability to act as pour point depressant since it can withstand low temperature condition, which is below 0°C

(Totten, 2003). High molecular weight PMA can act as both PPD and viscosity modifier.

2.1.2 Development of PPD

In the oil field application, chemicals of PPD were added into the oil tube or annular space, or squeezed into the oil formation so that the deposition of paraffin and asphaltene was inhibited. According to Machado et.al (2001), they was studied on influence of the EVA vinyl acetate content on the viscosity and pour point. The performance of EVA copolymers as pour point depressant strongly depends on the copolymer composition and the best efficiency at optimum concentration. The traditionaly used macromolecule type's inhibitors are not as good as mixing products of macromolecules, polycircle aromatic hydrocarbons, polar organic compounds and various surfactants (such as wetting agents, disperssants and so on). Hence, they come out emulsion pour point depressant. Emulsion pour point depressant proved to be an efficient way to inhibit wax deposition. According to Chen et.al (2010), they have found that, pour point depressants that has been treat will interrupt the structure of paraffin. After that, the paraffin mixtures was partially transformed from orthorhombic into hexagonal form. So that, additive of PPD is important in prevention wax crystal growth and play role of lowering the melting point of wax.

2.1.3 Mechanism of Pour Point Depressancy

The mechanism of paraffin dispersant is to penetrate into wax oil gel, be adsorbed on individual particle, and reduce the tendency of wax particles to stick together. Alternatively, the dispersants may adsorb on the inner surface of a pipeline and reduce the ability of wax to adhere to pipe wall.

According to figure 2.2, the prevention mechanism of interlocking wax crystal by polymer additives. The mechanism to prevent agglomeration primarily involves the structure of the PPDs to disrupt the crystal habit of wax crystals. The structure involved in this process are the pendant chains, which use to cocrystallize with the wax and the polar end groups. These groups are responsible for disrupting the orthorhombic crystal structure into a compact pyramidal form; this process prevents the crystals from agglomerating and forming a gel like structure to deposit on the pipeline surface, (Hemant et.al, 2008).

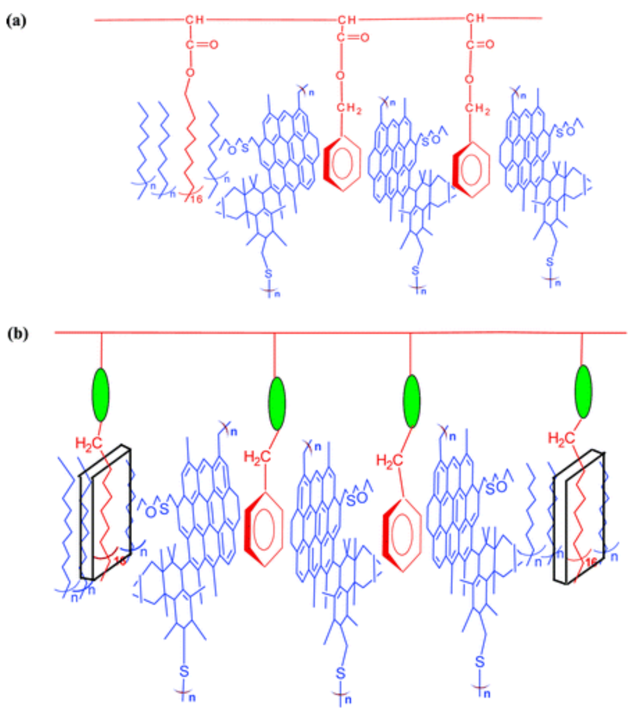

Figure 2.2: Prevention mechanism of interlocking wax crystal by polymer additives:(a)Nucleating site interaction (red) to asphaltene and wax molecules (blue), (b)Polar component of additive (green) hinder co-crystallization of asphaltenes and wax (Hemant et.al.2008).

PPDs are most popular flow improvers, which affect crystal growth, modify wax crystal structure and prevent the interlocking of wax crystals, enhances the flow properties of crude oil. It is believed that PPDs co-crystallize with wax, hence creating faults in wax crystal which change the shape and size of wax crystals and prevent the interlocking of crystals into different shape (Ali 2012).

According to (Souchik 2009), (refered Figure 2.3) illustrate the PPD function to control the wax crystallization phenomenon in two principal ways. First, delaying the formation of wax–gel matrix to significantly lower temperatures than would normally occur or reducing the viscosity contribution of the crystal wax particles. Second is the PPDs act by interrupting the three-dimensional growth of wax crystals.

Figure 2.3: Gel network of needle-like structure (Souchik 2009).

Figure 2.8 below show the function of PPD to prevent agglomeration primarily involves the structure of the PPDs to disrupt the crystal habit of wax crystals (refered Figure 2.4). The structure involved in this process are the pendant chains, which use to co-crystallize with the wax and the polar end groups. These groups are responsible for disrupting the orthorhombic crystal structure into a compact pyramidal form; this process prevents the crystals from agglomerating and forming a gel like structure to deposit on the pipeline surface, (Hemant et.al, 2008).

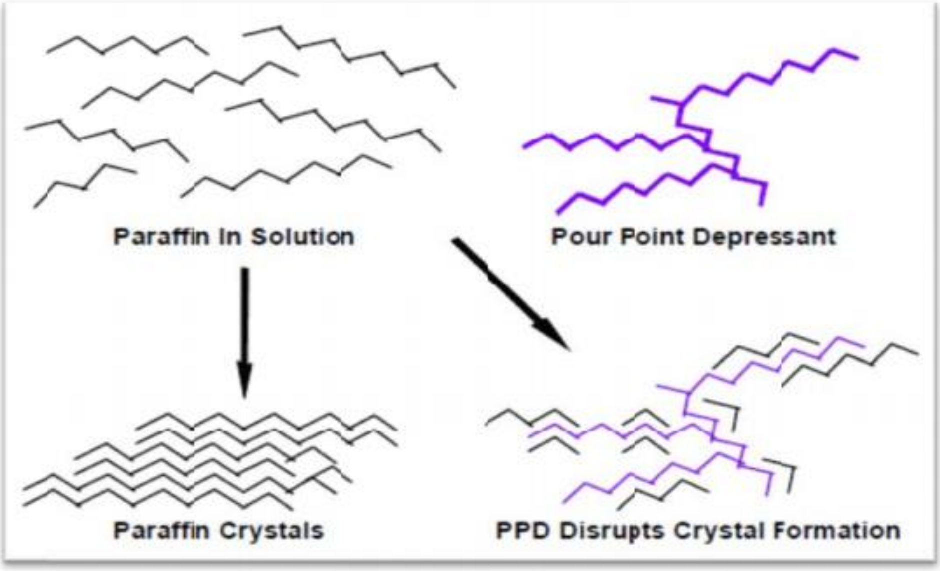

Figure 2.4: Effect of PPD disrupt the crystal habit of wax crystal (Ali 2012).

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 Zhang et.al (Zhang, Wu et al. 2003).

2.1.3.1 Adsorption and Co crystallization theory

Indication were the polymers function by coating the surface of the wax crystals and preventing further growth. The polymer either being absorbed into the face of the wax crystal if the PPD is co-crystallize with the wax crystal if it is comb polymer. Thus, the wax like components of the additive are incorporated into the wax crystal lattice and thus modify the morphology of the growing crystal (Pillon 2010). According to (Yang, Zhao et al. 2015), at temperatures near or below the WAT, many polymeric Wax Inhibitors and PPDs co-crystallize with wax molecules or adsorb on growing surfaces of precipitated wax crystals. Incorporation of polymeric Wax Inhibitors and PPDs into wax crystals disrupts growth, inhibiting wax deposition, and improving flow ability. Molecular dynamic (MD) simulation has been used to investigate the effect of polymeric Wax Inhibitors and PPDs on the growth of wax crystals.

2.1.3.2 Nucleation theory

The additive heterogeneously nucleates the wax crystals and this result in crystals of relatively smaller size (Pillon 2010). According to (Yang, Zhao et al. 2015), at temperatures well above the WAT, certain polymeric WIs and PPDs self-assemble into micelle-like aggregates exhibiting a crystalline core and soluble hairy brushes surrounding the core, creating a larger number of subcritical size wax nuclei (so-called poly nucleation). Partially shielded nuclei reduce super saturation, reduce crystal growth rates, and facilitate the formation of more abundant smaller wax crystals. Wax crystal size reduction facilitates inhibition and rheological beneficiation.

2.1.4 Emulsion PPD

Traditional PPD solidified at room temperature, when a PPD of acrylate polymer (Trade name: PD90) is solvent based PPD, even it has strong polymer-solvent interaction but low melting point of around 45°C which will make it solidify at room temperature (Admiral, Abdullah et al. 2016).

Hence, emulsion technique have been apply to create emulsified PD90 to form fine droplets of PPD but still lack in their properties performance, then Nano hybrid pour point depressant (NPPD) was introduced to improvise their properties in term of electrical properties, optical properties and mechanical properties.

Emulsion has been viewed by (Sagalowicz and Leser 2010), they have been applied emulsions system into food industry for stabilizing the nutrition and health (refered Figure 2.5), improving test and aroma impact on food texture. Same as (McClements 2015), he have found that emulsions is the kinetically stable (metastable) for a certain period time (a few days, months, or years) by including the substances such as stabilizer.

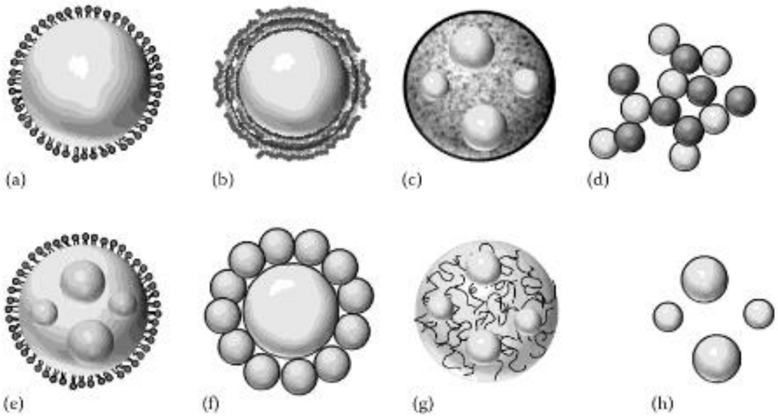

Figure 2.5 : Structural of emulsions base-systems that been used in foods(McClements 2015).

On the other hand, in PPD chemical production, emulsions technology been less explored and exposed in this area since there are only a few studies regarding PPD emulsions product. According to (Admiral, Abdullah et al. 2016), they have found that emulsions behaviour improved PPD flow ability such as freezing point, viscosity at room temperature, particle size and zeta potential of the emulsified products. In addition, introduce the EVA copolymer emulsions in PPD has been optimized the stability of the emulsions (Rosdi, Ariffin et al.).

Emulsion PPD need to blend with nano particles material such as grapheme and grapheme oxide to improve their mechanical and thermal properties.

2.2 Polymer NanoComposites

2.2.1 Overview of Polymer Nanocomposite

Polymer nanocomposites are polymer matrices reinforced with nano-scale fillers (Mai and Yu 2006). This new class of composite materials has shown the enhanced optical, electrical and dielectric properties. According to Roy et.al (2005), nano-particle filled polymers provide resistance to degradation and it improve the thermo-mechanical properties without causing a reduction in dielectric strength.

Nano hybrid polymeric material consist of a polymer or copolymer that having the nanoparticles dispersed in the polymer matrix. Earlier studies have shown that nanoparticles dispersed in different matrixes, Gojny et.al (2005). Thus, it give impact on the degree of crystallization and heat distortion temperature. Furthermore, the physical properties of these matrixes significantly affected by their size geometrical shape, interaction nature, and dispersion degree.

According to (Lloyd and Lave 2003), the mixing of polymers and nanoparticles will cause the enthalpic and entropic interaction is happen between layered of polymer and nanoparticles to control the macroscopic performance of the material. (Refered figure 2.6), combination of polymer and nanoparticles will form intercalated nanocomposite and exfoliated nanocomposite.

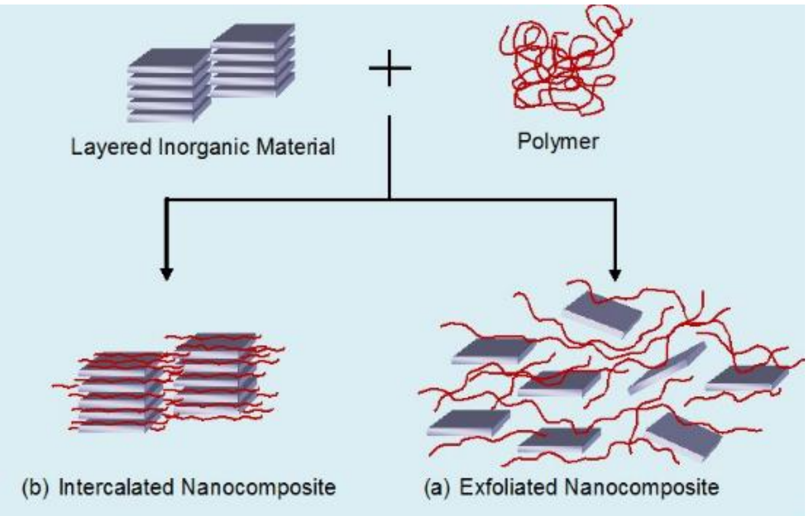

Figure 2.6: Schematic structure of nanocomposite formed by combining polymer and layered inorganic material (Lloyd and Lave 2003).

The comparison between nanocomposite and microcomposite polymer materials have been done based on three major properties, which is content of fillers, size of fillers, specific surface area of fillers (Tanaka, Montanari et al. 2004).

Table 2.1: Comparison between microcomposites and nanocomposites (Tanaka, Montanari et al. 2004).

Properties	Microcomposite	Nanocomposite
Filler content	>50wt%	<10wt%
Filler Size	10^{-6}m	10^{-9}m
Specific surface area of fillers	Small	Large

In addition, the nanoparticles can greatly affect the heat distortion and crystallization temperature, and the final size of polymer nanocomposites. The both geometry and dispersion of nanoparticle or sheets in the polymer as well as the type of interaction (covalent or physical) with polymer matrixes defined the physical properties of the polymer Nano hybrid.

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2.2.2 Characteristic of Polymer Nanocomposite

Polymer Nanocomposite consists of partial discharge that can improved the mechanical, physical and electrical properties of polymers. For instance, graphene and graphene oxide (GO) play a important role in providing a good improvement application in polymer properties. Nanocomposite have a specific area that is three orders larger than microcomposites.

The polymer nanocomposite is the exceptional material because of fibre like structure of carbon nanotubes, low density, high aspect ratio, and extraordinary mechanical properties make them particularly attractive for reinforcement in composite materials. The high aspect ratio of the nanotubes coupled with a strong intrinsic van der Waals attraction between nanotubes combine to produce ropes and bundles of CNT. According to (Moniruzzaman and Winey 2006), they have found that functionalization of nanotubes provides a convenient route to improve dispersion and modify interfacial properties that can improve the properties of nanocomposites. Nanotubes is the conductive fillers in polymer nanocomposites. Further advances with respect to electrical conductivity in nanotube or polymer composites.

According to Izzati et.al (2014), the inteaction zone and interfacial area is the main factor to the improvement of the insulating properties of the nanocomposites. It is due to the area that interface between the polymer matrix and the nanofillers. The specific surface area that is the three larger than conventional microcomposite filler provides the smaller distances between neighboring fillers. Nanoparticles have a high surface area-to-volume ratio, which means for the same particles loading, a nanocomposites will have a much greater interfacial area than microcomposites.

Nanocomposite with nano size particles improve the barrier resistance against gas and liquid permeation. Nanoparticles have been alter the polymer structure (refered Figure 2.7) to have a barrier behaviour between their layer structure and the changes anisotropic ionic conductivity between layers (Cao, Irwin et al. 2004).

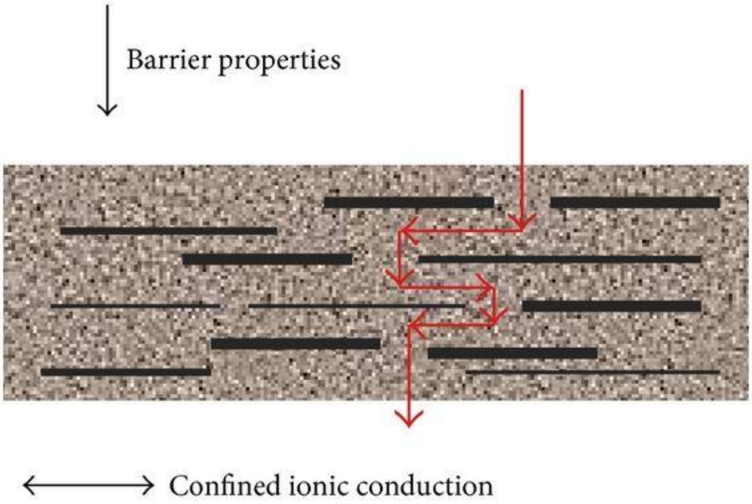

Figure 2.7: The barrier behaviour of the nanoparticles inside polymer matrix (Cao, Irwin et al. 2004)

2.2.3 Advancement of Polymer Nanocomposite

Polymer nanocomposite consist of carbon nanostructures which excellent microwave. Thus, in biomedical field they have been innovate the Nanocomposite Hydrogel for on demand drug delivery. The combination of this material (Refered Figure 2.8) can promote the response of hydrogels to a new stimulus that can mobile in versatile ways. Moreover, the hybrid system enable routes of drug with limited systematic absorption. However, hydrogels provide nanoparticles with the clinical useful formulation and needed for clinical application.

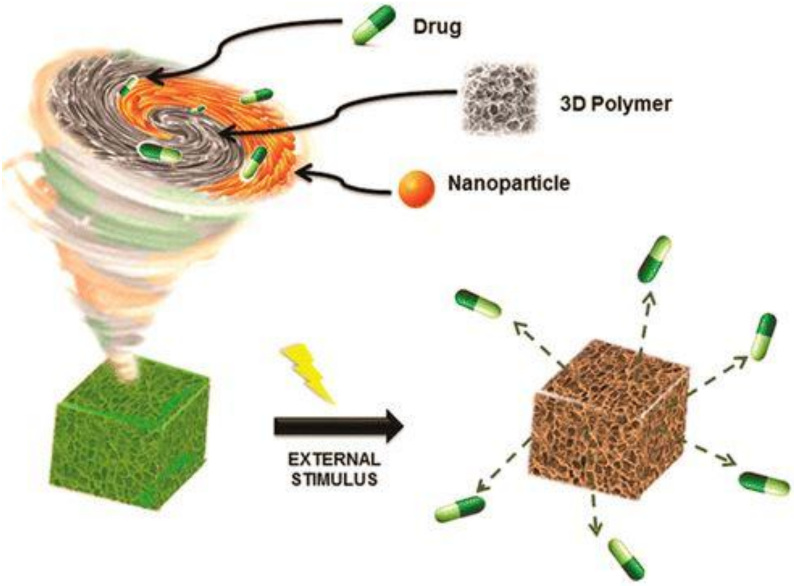

Figure 2.8: Schematic illustration showing the combination of nanoparticle with 3D polymer and drug improved the drug delivery (Izzati, Arief et al. 2014).

In this project, graphene have been choose and used for further research work. It is because graphene is one of the nanoparticles that has the exceptional properties and it will reduce the costing. Graphene can improvise the properties behaviour of Nano-hybrid Pour Point Depressants since it can be modify the polymer structure of acrylate polymer through the interaction between acrylate polymer, graphene and van der Waals forces.

2.3 Nanoparticles

2.3.1 Overview

Nanoparticles exist in variety field of technology since it have the exceptional properties. One most familiar, it have been apply in biomedical field to produce anticancer. Gryparis et.al (2007), investigate the in vitro anticancer activity of cisplatin-loaded PLGA-mPEG nanoparticles on human prostate cancer cell. The nanoparticles that they used is PLA-mPEG. They modified nanoparticles through double emulsion layer. The result successfully proved that, by using nanoparticles material, it help to loaded with cisplatin entered the cells.

2.3.2 Graphene

2.3.2.1 Introduction to Graphene

L. Changgu et al. (2008) have found that, graphene is the exceptional material when it has two-dimensional (2D) sheet of covalently bonded carbon atoms (as shown in figure 1), forms the 3D graphite and 1D carbon nanotubes. Graphene has a great attention because it consists a special properties since single atom packed in the hexagonal crystal lattice, but it poor solubility in aqueous and non-aqueous solution. The suggestion ways that can solve this problem by modified chemical of graphene with some oxidant to form graphene oxide. Graphene in water (refered Figure 2.9) is typically negatively charged, this may be modelled as an electric double layer (EDL), in which there are three distinct regions which is a closely bound layer of oppositely charged ions (Stern layer), a diffuse layer and then the bulk solvent Johnson et.al(2015).