SURFACE INTERACTIONS OF POLYMER NANOPARTICLES IN WAXY CRUDE OIL MODEL SYSTEM

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled: "**Surface Interactions of Polymer Nanoparticles in Waxy Crude Oil Model System**". 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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LIST OF SYMBOLS

μ_e	Electrophoretic mobility
a	Radius of particles
e	Elementary charge, $e = 1.602 \times 10^{-19}$ C
f(κa)	Henry's function
Z	Surface charge of the colloid suspension
ε	Dielectric constant
ζ	Zeta potential
η	Viscosity of the carrying solvent
κ	Debye length
T_m	Melting temperature
T_c	Crystallization temperature
ΔH_m	Heat of melting
ΔH_c	Heat of crystallization

LIST OF ABBREVIATIONS

AOT	Aerosol-OT
ATR	Attenuated Total Reflectance
CMC	Critical Micelle Concentration
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared Spectroscopy
GO	Graphene oxide
KPS	Potassium persulfate
MMA	Methyl methacrylate
PMMA	Poly (methyl methacrylate)
PPD	Pour Point Depressants
SDS	Sodium dodecyl sulphate
SMMRE	School of Materials and Mineral Resources Engineering
USM	Universiti Sains Malaysia
UV-Vis	Ultraviolet–Visible Spectroscopy
WAT	Wax appearance temperature

ABSTRAK

Kini, penyumbatan minyak lilin dalam saluran paip adalah isu yang paling mencabar untuk diselesaikan yang menjejaskan banyak syarikat minyak dan gas sejak tahun 1920-an, disebabkan oleh suhu rendah saluran paip bawah laut yang menyebabkan fenomena penghabluran lilin yang tidak diingini. Matlamat kajian ini adalah untuk menilai kesan kepekatan natrium dodesil sulfat (SDS) ke atas kestabilan emulsi poli(metil metakrilat)-graphene oksida (PMMA-GO), untuk menciri dan mengenal pasti interaksi permukaan PMMA-GO dan untuk mengkaji prestasi PMMA-GO pada penstabilan minyak dengan menilai interaksi permukaan dalam sistem kelikatan yang berbeza. PMMA-GO disintesis melalui pempolimeran emulsi dengan ultrasonik yang mempunyai jumlah tetap pemula kalium persulfat (KPS) dan kepekatan graphene oksida (GO) dan natrium dodesil sulfat (SDS) yang berbeza-beza dari julat 0.1 hingga 1.0 wt%. Sampel dicirikan menggunakan analisis spektroskopi inframerah transformasi Fourier (FTIR), analisis "Ultraviolet-Visible Spectrophotometry" (UV-Vis), Analisis Saiz Zarah, analisis Potensi Zeta dan analisis Kalorimetri Pengimbasan Beza (DSC). Bagi peringkat aplikasi, prestasi PMMA-GO pada penstabilan minyak akan dinilai menggunakan analisis Potensi Zeta dengan menggunakan heksana dan dekana sebagai sistem model minyak mentah. Kami didapati bahawa peningkatan kepekatan SDS dan GO menggalakkan kestabilan emulsi yang lebih baik apabila potensi zeta meningkat serta mempunyai kestabilan haba yang baik. Kepentingan kajian ini akan memberi maklumat penting tentang pendekatan untuk menghalang penghabluran lilin minyak mentah melalui interaksi permukaan nanopartikel polimer dan pada masa yang sama, meningkatkan kestabilan emulsi.

SURFACE INTERACTIONS OF POLYMER NANOPARTICLES IN WAXY CRUDE OIL MODEL SYSTEM

ABSTRACT

At present, the clogging of wax in pipelines is the most challenging issue to solve, which affecting numerous oil and gas companies since 1920s, due to the low temperature of subsea pipelines which caused undesired phenomenon of wax crystallization. The aim of this study is to evaluate the effect of sodium dodecyl sulphate (SDS) concentration on the stability of poly(methyl methacrylate)-graphene oxide (PMMA-GO) emulsions, to characterize and identify the surface interaction of PMMA-GO and to study the performance of PMMA-GO on oil stabilization by evaluating the surface interaction in different viscosity system. The PMMA-GO is synthesized via emulsion polymerization with ultrasonication having a fixed amount of potassium persulphate (KPS) initiator and varying concentrations of graphene oxide (GO) and sodium dodecyl sulphate (SDS) from range of 0.1 to 1.0 wt%. The samples were characterized using Fourier transform infrared spectroscopy (FTIR) analysis, Ultraviolet-Visible Spectrophotometry (UV-Vis) analysis, Particle Size Analysis, Zeta Potential analysis and Differential Scanning Calorimetry (DSC) analysis. For the application stage, the performance of PMMA-GO on oil stabilization will be evaluated using Zeta Potential analysis by applying hexane and decane as a crude oil model system. We discovered that the increasing SDS and GO concentration promotes better stability of emulsion as the zeta potential increases as well as having good thermal stability. The significance of this study will give vital information on approaches to inhibit wax crystallization of crude oil by means of surface interaction of polymer nanoparticles and at the same time, improve the emulsion stability.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The present research is a study of wax deposition that occurred in the crude oil whereby it influences the crude oil flowability along the pipelines and has been affecting the oil and gas industries since the 1920s. Wax deposition implies the formation of a layer of separate solid phase and the subsequent growth of this layer on a surface in contact with the crude oil. The formation of wax deposits can take place from an already precipitated solid phase, known as wax, through mechanisms of shear dispersion, gravity settling and Brownian motion, or from dissolved wax molecules through a molecular diffusion mechanism (Huang *et al.*, 2014; Theyab, 2018).

The wax crystallizations take place when the temperature of the flowing fluids is less than or equal to the cloud point or wax appearance temperature (WAT). Moreover, the term wax deposition refers to the formation and growth of a layer of precipitated wax crystal on the surface (Makwashi *et al.*, 2021). The main mechanism responsible for the wax precipitation includes the nucleation, growth and agglomeration. These processes often occur separately or continuously, with one stage always predominating at a time. The subsequent step results in the creation of a robust network in the system due to the interlocking of wax crystals (Yang *et al.*, 2015).

In extreme cold temperature of the deep sea, solidified crude oil could result in a serious blockage in the pipeline and leads to the interruption of the whole operation of the production plant. The major reason that induces the wax deposition process is the low temperature caused by the vulnerable subsea pipelines (Theyab, 2018). Wax deposition along with the pipelines increases as the temperature difference between the bulk of wax solution and the cold surface of the pipe increases (Singh et al., 2000). Therefore, the wax deposition must be avoided in the very first circumstances and removed after it has formed. Wax deposition in oil and gas production systems can be minimized or prevented using one or a combination of chemical, mechanical, and thermal mitigation approaches (Woo et al., 1984).

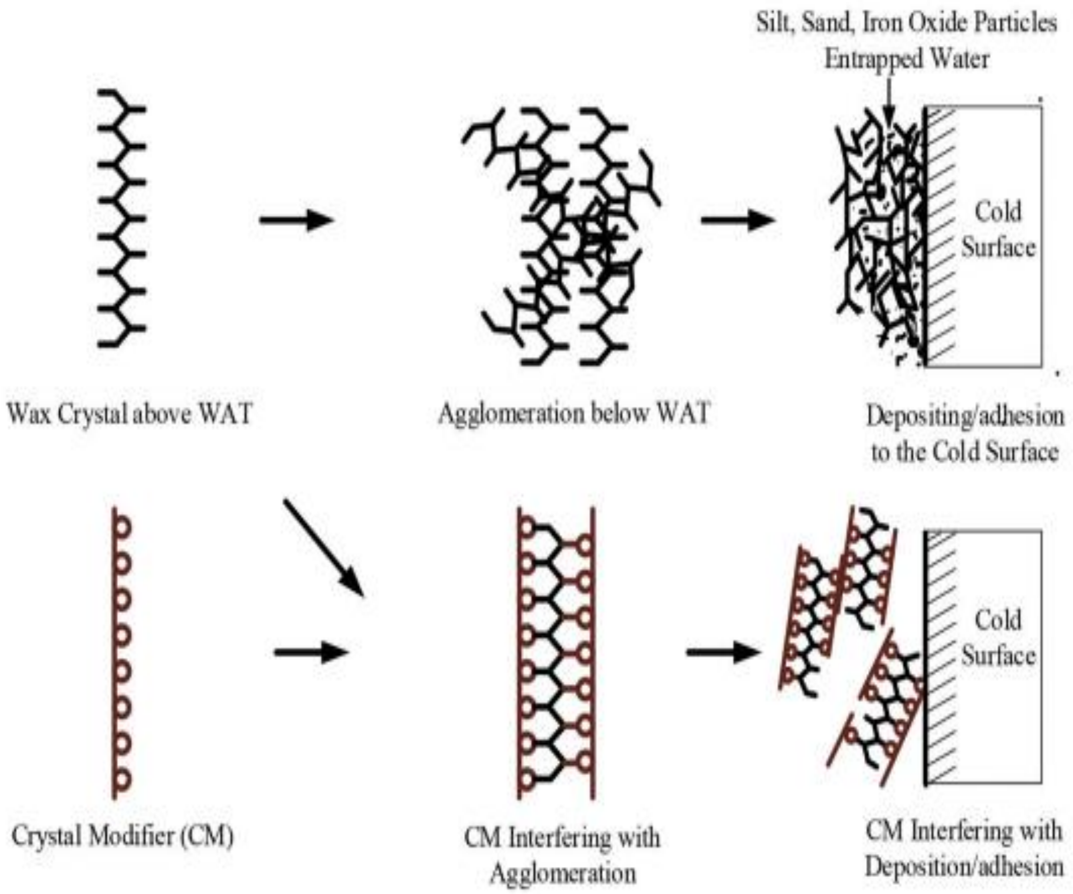

Figure 1. 1: Interaction mechanisms between wax crystals modifier with wax crystals (Adapted from Allen and Roberts, 1978, cited by Makwashi *et al*., 2021).

Currently, chemical mitigation methods using chemical additives such as wax deposition inhibitors and crystals wax modifiers (Figure 1.1) are becoming more prevalent (Adeyanju & Oyekunle, 2013) since they can cover long distances from crude oil flow lines. The application of mechanical and thermal mitigation methods involving offshore drilling and ocean floor completions is less preferable as it was economically prohibitive with the advent of extremely deep-sea production. Thus, chemical additives are the best option for wax deposition in pipelines. Chemical inhibitors have been used to minimize or prevent wax deposition in crude oil pipelines. It can be divided into four types of classes which include pour point depressants (PPD), crystal modifiers, dispersants, and solvents to treat the wax aggregation (Theyab, 2018).

Pour point depressants (PPD) are a chemical additive used in small amounts to allow oil to flow at very low temperatures (Howard, 2014), whereby it modifies the wax crystal size and shape, as well as inhibits the aggregation of wax crystals (Holder and Winkler, 1965). It is also known as a paraffin inhibitor which is capable to distort and modify the wax crystal structure during the deposition process along the crude oil pipelines. Specifically, PPDs interfere with or prevent the mechanism of molecular diffusion of deposition from taking place. It also modifies the wax crystals structures which were precipitated into small, highly branched structures having low cohesive properties.

Currently, there are three most common wax crystals modifiers, which are being utilised in the crude oil industry, in these groups, mainly copolymers namely (1) Group A: copolymer of ethylene vinyl acetate (EVA), a type of elastomeric polymer having ethylene and vinyl acetate segments, (2) Group B: copolymer having C18 through C22 methacrylate which has straight or branched alkyl esters of methacrylic acid and finally, (3) Group C: copolymer of olefin/maleic anhydride esters having dicarboxylic acids as functional group.

Nanohybrid pour point depressants (PPD) consisting of polymer and inorganic nanoparticles such as graphene derivatives, especially graphene oxide, have been widely studied in the last decade because these materials possess exceptional mechanical, thermal, and gas barrier, electric, and flame-retardant capabilities (Ying et al., 2014). Poly (methyl methacrylate) (PMMA) is one of the most common polymeric wax crystal modifiers used in the petroleum industry recently (Olajire, 2021). These polymer nanoparticle additives are utilized for flow optimization of crude oil since these additives are capable of co-precipitate with wax, creating steric hindrance during the crystallization process and interfering with the wax crystal growth and aggregations (Deshmukh & Bharambe, 2008; Steckel et al., 2022).

Recently, researchers have shown more interest in investigating polymer nanoparticles due to their significant performance as a chemical inhibitor to inhibit wax deposition (Jaberi, 2020). The usage of conventional polymers, such as poly(methyl methacrylate) (PMMA), has its shortcomings due to its thermomechanical properties compared to the other type of polymers (Theyab, 2018). Consequently, endless works done by scientists have been put into enhancing the properties of polymers by searching the suitable nanoparticles.

For this study, PMMA was chosen as the main polymer-based component, which was enhanced with the addition of graphene oxide. The use of poly(methyl methacrylate) PMMA alone to inhibit wax aggregation does not promise enough good results, and recent studies performed by researchers discovered that a highly oil-dispersed PMMA nanohybrid displayed good performance of the influence on the apparent viscosity of Egyptian crude oil (Al-Sabagh et al., 2016).

Furthermore, recent findings showed that the nanocomposite PMMA-GO has good suitability as PPD (wax inhibitor) for Indian waxy crude oil (Sharma et al., 2019). This can be explained because the oxidised graphene, GO, having oxygenated functional groups on its surface acts as a possible site for polymerization (Kumar et al., 2016), although it tends to agglomerate easily in dispersion (Ma et al., 2010). Moreover, GO sheets have the interesting benefits whereby it has the ability to create conductivity area and polarizability when it is being incorporated with polymer matrix (Zhang *et al.*, 2012).

The graphene oxide having 2D flexible sheets creates the smooth coating of the particles, and the oxygen functional group also offers amphiphilic properties to the hydrophobic carbon basal (Cote *et al.*, 2010). This gives an opportunity to stabilize emulsion droplets between two immiscible phases eventually synthesize the particles coated with GO via pickering emulsion polymerization process (Min, Lee and Choi, 2018). Therefore, there is a need to investigate the GO dosage optimization in PMMA-GO emulsion as PPD.

Figure 1. 2: Schematic illustration of emulsion polymerization of PMMA-GO.

Although different types of polymeric nanoparticles have been investigated for wax crystallization inhibition, the potential application of PMMA-GO with respect to the effect of anionic surfactant sodium dodecyl sulphate (SDS) concentration for waxy crude oil model crystallization inhibition has not yet been studied in the available literature. The incorporation of water-soluble SDS as anionic surfactant can significantly reduce the interfacial tension between two immiscible liquids due to the presence of amphiphilic molecules in the chemical structure of SDS surfactant and thus, SDS enhances the incorporation of GO sheets to promote better emulsion stability of polymer nanoparticles PMMA-GO. Therefore, the purpose of this research is to uncover the potential of laboratory synthesized PMMA-GO with different anionic SDS surfactant concentration on the performance of the waxy crude oil model system by evaluating the surface interaction in different viscosity system of crude oil model.

In this case study, PMMA-GO is synthesized by emulsion polymerization with ultrasonication having a fixed amount KPS initiator with varying concentrations of GO and SDS anionic surfactant from 0.1 to 1.0 wt%. The synthesized PMMA-GO and controlled PMMA were characterized using FTIR analysis, UV-Vis analysis, Zeta Potential analysis, particle size analysis and Differential Scanning Calorimetry (DSC) analysis. The performance of PMMA-GO on oil stabilization is studied using Zeta Potential analysis with decane and hexane as a crude oil model system.

1.2 Problem Statement

In the oil and gas industry, the clogging of wax in pipelines is the most challenging issue to solve which affected numerous oil companies around the world from the 1920s till the present day. Wax crystallization (also called wax deposition/aggregation) of the crude oil occurred because of many factors. One of the main factors is the low temperature caused by the cold and deep subsea pipelines that resulted in the low fluid temperature of the crude oil. When the fluid temperature of the crude oil drops below the wax appearance temperature (WAT), the formation of wax crystals took place. The wax crystallizes as it grows and further develops a 3-D network of wax aggregates (Yang *et al.*, 2015; Theyab, 2018). This later caused wax deposition and flow restrictions, which increases the viscosity of the fluid and further increased the pressure in the pipelines. In the worst-case scenario, it can cause a serious blockage in the pipeline and lead to the disruption of the whole production plant. Hence, the addition of polymer nanoparticles as a chemical inhibitor to the waxy crude oil model emerges recently acting as a potential wax treatment and flow enhancer using surface interaction concerning this issue.

Pour point depressants (PPD) can be utilized to permit the oil to flow at a very low temperature as it modifies the wax crystal size and shapes, reduces the interlocking forces between the two nuclei of wax molecules and deforms the regular crystal growth. PMMA-GO is one of the nanohybrid PPDs which can be applied for this wax deposition and flow assurance problem. The synthesis of PMMA-GO was carried out via emulsion polymerization using sodium dodecyl sulphate (SDS) as an anionic emulsifier and potassium persulphate (KPS) as an initiator. The emulsion procedure was employed for the polymerization of polymeric materials to generate chemical additives functionalized as a control for the formation of crystal paraffin wax in the majority of traditional PPD preparations. Traditional PPDs used to cure crude oil have a greater pour point than nanohybrid PPDs. However, there are gaps in research study between electrostatic interactions and wax crystallization that might impact when treated with crude oil to regulate the deposited paraffin wax.

Although PPDs with nanohybrids offer several benefits, the wax appearance temperature (WAT) is not included at low temperatures, which are temperatures below 0 °C. Cold flow may occur despite the presence of nanohybrid PPDs due to the production of paraffin wax crystals at lower temperatures. Thus, the flowability of treated crude oil with nanohybrid PPDs may be studied at low temperatures as low as 0 °C or as low as -20 °C.

The synthesized PPD, PMMA-GO tends to form agglomeration and graphene oxide deposition and indicates the instability of PMMA-GO emulsions. As a consequence, this creates an uncontrollable surface interaction between molecules of polymer nanoparticles in emulsion solution. Thereby, the incorporation of water-soluble SDS as an anionic surfactant is believed to significantly reduce the interfacial tension between two immiscible liquids due to the presence of amphiphilic molecules in the chemical structure of SDS surfactant and thus, SDS enhances the incorporation of GO sheets to promote better emulsion stability of polymer nanoparticles PMMA-GO. Hence, this study will explore the correlation between the concentration of SDS and GO upon the emulsion stability of synthesized PMMA-GO.

1.3 Research Objectives

Today, chemical methods, by means of polymeric nanoparticles, are preferred to rectify this issue as it was expected to yield a promising outcome, as well as gives lower costs of operations and reduce the labor work required. The objectives of this study are the following.

i. To evaluate the effect of SDS concentration on the stability of synthesized PMMA-GO emulsions
ii. To characterize and identify the surface interaction of the synthesized polymer nanoparticles, PMMA-GO
iii. To study the performance of PMMA-GO on oil stabilization by evaluating the surface interaction in different viscosity system.

1.4 Thesis Outline

This thesis consists of five chapters which discuss on PMMA-GO as nanohybrid pour point depressants used to improve the flow restrictions of waxy crude oil in the deep-sea pipelines. Brief descriptions of each chapter were elaborated as follows.

Chapter 1 explains the introduction of the research background of the study. This chapter also highlights the problem statements of the study, research objectives, outline of the thesis and research plan.

Chapter 2 discusses the literature review of the research study. This literature review covers waxy crude oils, introduction to Pour Point Depressants (PPD), mechanism of Pour Point Depressants (PPD), introduction to acrylic polymers and emulsion polymerization process, mechanism of emulsion polymerization of PMMA, the role of graphene oxide as polymer nanoparticles in PPD, the effect of surfactant dosages in emulsion polymerization of PMMA-GO, surface interaction of waxy crude oil and PPD, wax stability in low temperature, electrophoretic mobility in zeta potential and colloidal stability theory and finally, application of PMMA-GO as Pour Point Depressants (PPD).

Chapter 3 briefs about the methodology of this research study. All the details of materials, machines, flowcharts, methods, testing and characterizations for this research study were presented in this chapter.

Chapter 4 focuses on the results and discussions of the research study. This includes the results for the characterization of FTIR analysis, UV-Vis analysis, Particle Size Analysis, Zeta Potential analysis and Differential Scanning Calorimetry (DSC) analysis. This chapter also aims to discuss the performance of crude oil stabilization upon application of nanohybrid PPD synthesized, PMMA-GO, using Zeta Potential analysis.

Chapter 5 concludes with the findings and significance of the research study. There are also a few suggestions, improvisations and recommendations that can be utilized in future work.

1.5 Research Plan

At present, the clogging of wax in pipelines is the most challenging issue to solve, which affecting numerous oil and gas companies since the 1920s. This undesired phenomenon of wax crystallization occurred because of the low temperature of subsea pipelines. This study aims to develop a polymer nanoparticles particularly, poly (methyl methacrylate)-graphene oxide, PMMA-GO, evaluate the effect of SDS concentration on the stability of synthesized PMMA-GO emulsions and study the performance of PMMA-GO on crude oil stabilization to inhibit wax deposition issues and prevent flow restrictions using an oil model system.

The PMMA-GO is synthesized via emulsion polymerization with ultrasonication having a fixed amount of KPS initiator with varying concentrations of GO and anionic surfactant SDS from range of 0.1 to 1.0 wt%. The deionised water has been used as a dispersed medium in the nano-emulsion system for characterization purposes. Afterwards, the synthesized PMMA-GO and controlled PMMA were characterized using FTIR analysis, UV-Vis analysis, Particle Size Analysis, Zeta Potential analysis, and Differential Scanning Calorimetry (DSC) analysis. For the application stage, the performance of PMMA-GO on oil stabilization will be evaluated through Zeta Potential analysis using hexane and decane as a crude oil model system.

It was expected that the oil incorporated with PMMA-GO varying concentrations of GO and anionic surfactant SDS will reduce the wax aggregation by hindering the wax crystal growth using surface charge interaction between the oil model and polymer nanoparticles. This will disrupt the wax morphology and change the nature of the crystallization growth structure. Furthermore, by employing the electrostatic stability theory, the relationship between electrophoretic mobility, particle size, particle stability and zeta potential can be determined. Increasing dosages of SDS and GO promotes better stability of emulsion as the zeta potential increases. The faster the time is taken for the particles to coagulate (particle coagulation), the narrower the distribution of the particle size whereas the longer the extent of particle coagulation, the larger the average particle size of the wax aggregates. Hence, this results in a reduction of viscosity of polymer nanoparticle-oil dispersion.

The significance of this study will contribute vital information on approaches to inhibit and/or reduce wax crystallization of crude oil model using surface interaction of polymer nanoparticles with respect of SDS and GO concentration and at the same time, improve the rheological properties of the oil dispersion. This nanohybrid PPD will help to reduce the permeability during the charge and transportation process and improve the flow restrictions of the crude oil along the deep-sea pipelines as proposed based on the pour point mechanism and rheological properties between the nanohybrid PPD, PMMA-GO and the paraffin crude oil.

CHAPTER 2

LITERATURE REVIEW

2.1 Waxy Crude Oil

Crude oil is a complex fluid and mostly contains wax, asphaltene, resins, and light hydrocarbons that are aliphatic and aromatic (Maleki et al., 2021). One of the constituents of crude oil is the paraffin wax comprises of long-chain alkanes ranging from 16 to 64 carbon atoms or high molecular weight n-paraffins (Diaz and Theyab, 2017; Singh et al., 2000; Srivastava et al., 1993). The phase separation of paraffinic solids from crude oil is a major operational issue for the petroleum industry because the association of these wax crystals results in an extended network structure with characteristics similar to those of gels formed from dispersions of weakly attractive colloidal particles (Visintin *et al.*, 2008).

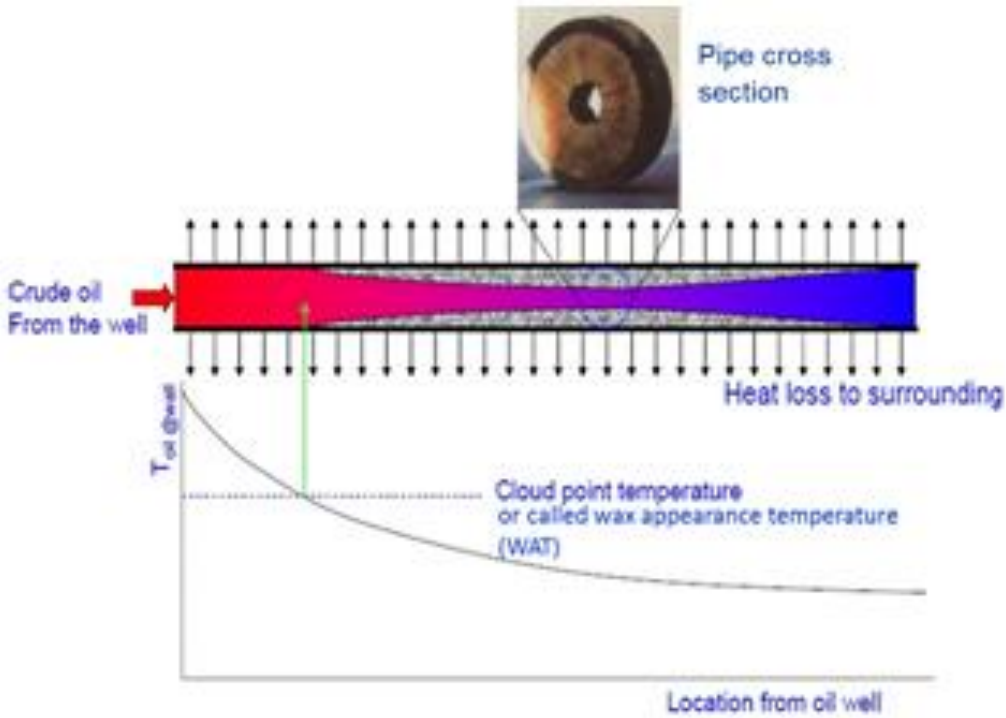

Figure 2. 1: Wax deposition process in the hydrocarbon pipeline (Theyab and Diaz, 2016).

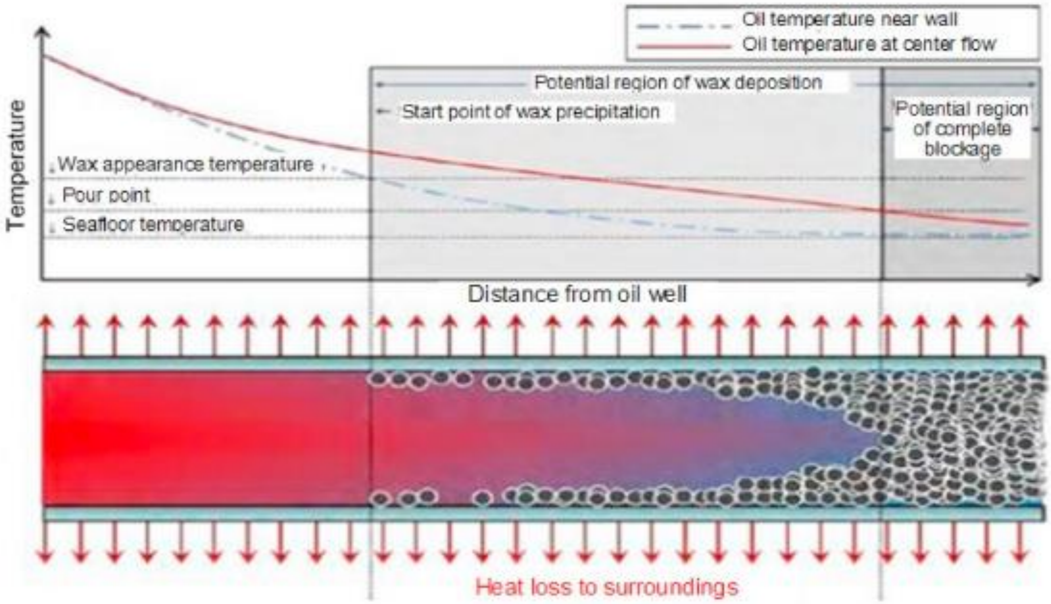

Figure 2. 2: Wax deposition process (Kang et al., 2014).

When the temperature of crude oil in the pipelines drops lower than the wax appearance temperature (WAT), formation of wax crystals takes place as shown in Figure 2.1 and Figure 2.2. Additionally, increasing the temperature difference between the cold surface and the wax solution will also contribute to increase the wax deposition. Wax deposition occurs when the surface temperature is below both the solution temperature and the solution cloud point (Theyab and Diaz, 2016). Besides previous conditions, wax formation can also occur when the dissolved wax molecules are formed through a molecular diffusion mechanism or can be formed from the existing precipitated solid phase of wax via (1) gravity settling; occurs due to the components of precipitated wax particles settled down towards the bottom of the pipe, (2) shear dispersion; occurs due to the components of precipitated wax particles dispersed towards the wall of the pipes, and (3) Brownian motion; occurs due to the components of precipitated wax particles diffuse towards the wall of the pipes (Huang *et al.*, 2016; Theyab, 2018). The precipitated wax on the pipe walls will start to form an incipient gel on the cold surface. These crystallized waxes grow and develop a three-dimensional network of crude oil wax aggregates, which trapped a significant amount of oil within it. As time progresses, the incipient gel grows, having a radial thermal and mass transfer gradient due to heat loss to the surrounding area (Wu *et al.*, 2012; Theyab, 2018).

Table 1. 1: Some examples of different solvent types and chemical inhibitors applied with their reduced WAT respectively

Solvent Type	**Chemical Inhibitor/ PPD**	**Reduced WAT (°C)**	**References**
Iranian crude oil	EVA-ZnO (500 ppm)	19.2	(Vakili *et al.*, 2021)
Iranian crude oil	EVA-MgO (500 ppm)	17	(Vakili *et al.*, 2021)
KSG#49 crude oil	W2001 (1500 ppm)	23	(Makwashi *et al.*, 2021)
Toluene/n-heptane (45/55) v/v%	EVA10 + asphaltenes	7.3	(D'Avila *et al.*, 2020)
Crude oil (9.8 wt% wax content)	GO-PEG (400 ppm)	32.2	(Jaberi, Khosravi and Rasouli, 2020)
Egypt crude oil	2% VTOP-BT-PODA-VL (500 ppm)	6	(Betiha, Mahmoud and Al-Sabagh, 2020)
China crude oil	Modified MMT-EVA (100 ppm)	15.3	(He *et al.*, 2016)
Egypt crude oil	PMMA-0.3%GO (500 ppm)	21	(Al-Sabagh *et al.*, 2016a)
Indian crude oil	PMMA-1%GO (1500 ppm)	23	(Sharma, Mahto and Vuthaluru, 2019a)

2.1.1 Pour Point Depressants (PPD)

There are three classes of techniques applied to solve wax deposition issues, which are predictive methods, which involve numerical simulation to identify and avoid conditions that can provoke wax precipitation; preventive methods, including heating production lines and using chemical inhibitors; and lastly, corrective methods, such as mechanical and chemical removal (Steckel *et al.*, 2022). Currently, corrective methods are generally used by the oil and gas industries worldwide but preventive methods by means of chemical inhibitors, started to gain more attention as it can reduce the operational disruption and shutdowns of the petroleum plant (D'Avila *et al.*, 2020).

Pour point depressants (PPD) are a chemical additive used in small amounts to allow oil to flow at very low temperatures (Howard, 2014), whereby it modifies the wax crystal size and shape, as well as inhibit the aggregation of wax crystals (Holder and Winkler, 1965). In other words, the depression takes place in pour point occurs due to the wax crystal modification. The PPD molecules are absorbed on various crystals faces, therefore reducing the interlocking forces between the two nuclei of wax molecules and deforming the regular crystal growth (Khidr, Doheim and O. A. A. El-Shamy, 2015) It was identified that the transition from plate-like to spherulitic crystal structure may be associated with the lowering of the pour point (Au, 2001). However, the wax crystals properties depend on the source of crude oil, as such, the oil is derived from waxy crude oil from the western desert crude oil, and among other factors, for example, the cooling rate and degree of agitation during the cooling process and so on (Khidr, Doheim and O. A.A. El-Shamy, 2015).

The composition of crude oil is one of the main factors that will significantly influences the wax deposition and PPD performance in viscosity reduction (Singhal *et al.*, 1991). Addition of PPDs to crude oil will resulted in a decrease of wax deposition and increase of crude oil flowability as the viscosity decreased (Wardhaugh and Boger, 1991).

2.1.2 Mechanism of Pour Point Depressants (PPD)

In order to avoid wax deposition in the oil pipelines, chemical treatment of waxy crude oil with chemical additives known as pour point depressants are widely implemented since electrical and mechanical procedures are inconvenient and uneconomic. Since the complexity of the crude oil properties depends on the source and the specificity of the PPD, there are several different types of PPDs for various types of crude oil have been established.

Ethylene and vinyl acetate (EVA) is one of the most popular PPD having excellent pour point depressants properties, superior performance and good adaptability and thus, EVA based PPD have been extensively utilised in the pipeline transportation of crude oil. Studies has consistently demonstrated that EVA molecules having polar molecules and non-polar molecules whereby the polar groups increase the repulsion effects for the deposition of waxy alkane molecules on the cold surface of pipelines and the non-polar groups have good affinity to the adjacent alkane waxy molecules (Machado, Lucas and González, 2001; Zhang *et al.*, 2004; Farazmand *et al.*, 2016). EVA based PPD resulted in significant reduction from 34°C up to 5°C (Jing, Ye and Zhang, 2017). It was observed that nanohybrid PPD causes a drastic improvements whereby it acts as nucleation centres which used to promote the wax crystallization. This leads to the wax crystals forming more dispersed and compact structured crystals and thereby, causing a weaker waxy crude oil network structure (Jing, Ye and Zhang, 2017; Huang *et al.*, 2021).

Recent studies proved that jointing polymers with nanoparticles can improve the inhibition efficiency of paraffin wax compared to the conventional polymer (Maleki et al., 2021). Apart from nucleation centres, it was also reported that the nanoparticles adsorption on wax crystals and solvent adsorption on the surface of polymers can hinder wax crystals growth and the formation of wax crystals network (Fu *et al.*, 2011). This causes the regular growth of wax crystals being rendered on different crystals faces as it decreases the overlapping phenomenon between the crystal wax nuclei (Khidr, Doheim and O. A. A. El-Shamy, 2015). Thus, the action of mechanisms of the PPDs have been described using nucleation, co-crystallization (Figure 2.3) and adsorption (Holder and Winkler, 1965; Betiha, Mahmoud and Al-Sabagh, 2020).

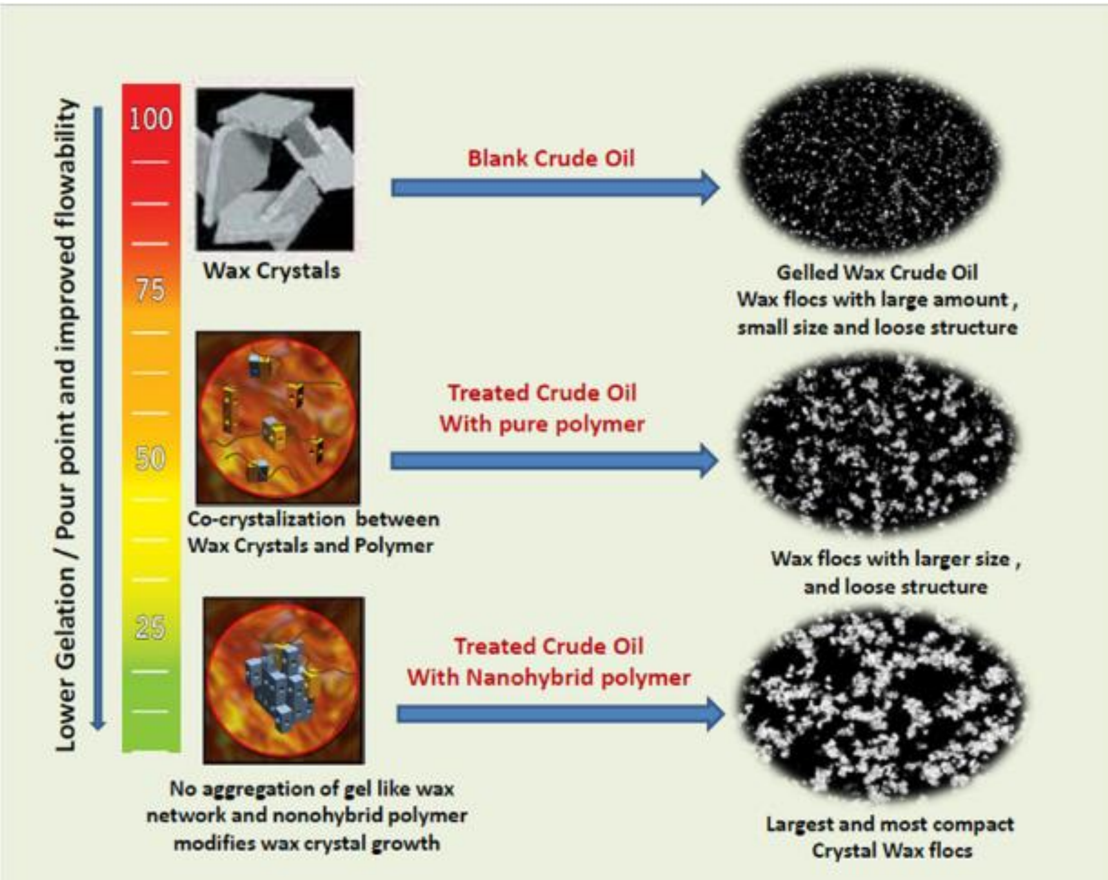

Figure 2. 3: Schematic illustration of the action mechanism of polymer as PPD in reducing gelation point or pour point and improving the flowability of crude oil (Betiha, Mahmoud and Al-Sabagh, 2020).

2.2 Acrylic Polymers and Emulsion Polymerization Process

Acrylic polymers are derivatives of acrylic or methacrylic acid, which are synthesized by chain growth mechanisms, especially free radical initiation (Odian, 1991; Walker, 1999). It is a tough, rigid, and transparent plastic materials which are available in a variety of colours and finishing for various applications such as electronics, lighting, automotive parts, and outdoor applications, specifically glazing in architecture and construction (Chan et al., 2020). Perspex ®, Acrylite ®, Europlex ®, Optix ®, Duraplex ® and Plexiglass ® are some of the trade names for acrylic polymers that can be found in the market. The primary monomers of acrylic polymers are ester-acrylate (R=H) groups and methacrylate (R=CH_3) groups (Figure 2.4) (Jalal Uddin, 2010). The characteristics of monomers and their polymers are determined by the nature of the R and R′ groups.

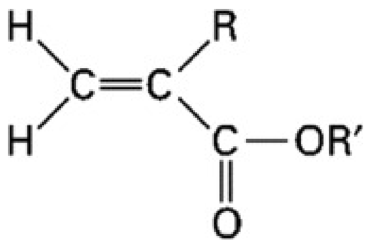

Figure 2. 4: Structure of acrylic ester (Uddin, 2010).

Poly (methyl methacrylate) (PMMA) is by far the most prevalent acrylic polymer. PMMA is a strong, optically clear material with excellent weather resistance, high thermal stability, and heat resistance (Theyab, 2018). Majority of commercial acrylic polymers have excellent UV stability. PMMA oxidizes when exposed to shorter UV wavelengths but not when exposed to solar UV despite having hydrogen atoms that are vulnerable to oxidation. PMMA can scarcely break down at temperatures below 200°C, when thermal and thermally oxidative decomposition temperatures are included. This also contributes to its weather resistant capabilities. Furthermore, PMMA exhibits low moisture absorption, good chemical resistance, and excellent dimension stability. Apart from that, it also has outstanding scratch resistance compared to other transparent plastics such as polycarbonate (Chan et al., 2020). PMMA also act as good polymer matrix and are extensively used in microfluids and studies regarding colloidal stability due to its good electrical properties, optical properties and mechanical properties (Khademi *et al.*, 2017).

Emulsion polymerization is a polymerization process that has a variety of commercial and academic uses. It requires an amphipathic emulsifier to emulsify hydrophobic polymers via the aqueous phase, followed by the production of free radicals using either water or oil soluble initiator. It is distinguished by a decrease in the bimolecular termination of free radicals as a result of free radical segregation among discrete monomer-swollen polymer particles. The latex particles varied in size from 10 nm to 1000 nm in diameter and were mainly spherical. A typical particle includes 1–10,000 macromolecules, with each macromolecule containing 100–106 monomer units (El-hoshoudy, 2018). Emulsion polymerizations have a wide range of applications such as coatings, thermoplastics, adhesives, binders, rheological modifiers, synthetic rubbers, plastic pigments, and many more (Chern, 2006).

2.2.1 Mechanism of Emulsion Polymerization of PMMA

Poly (methyl methacrylate), PMMA is a versatile polymer and has been utilized in a wide range of applications. It was discovered by German chemists, Fittig and Paul in 1877 in which polymerization of methyl methacrylate, MMA monomer produces poly (methyl methacrylate) (Lovell & El-Aasser, 1997). Emulsion polymerization involves the conversion of the emulsified mixture into a stable dispersion of polymer particles by a free-radical propagation mechanism. It contains the emulsification of monomers in a continuous aqueous phase, stabilization of the initial droplets and final polymer particles by a surfactant (Upadhyaya et al., 2012). For emulsion polymerization of PMMA, a water-soluble initiator reacts with the monomer into micelles and MMA is turned into polymerized PMMA.

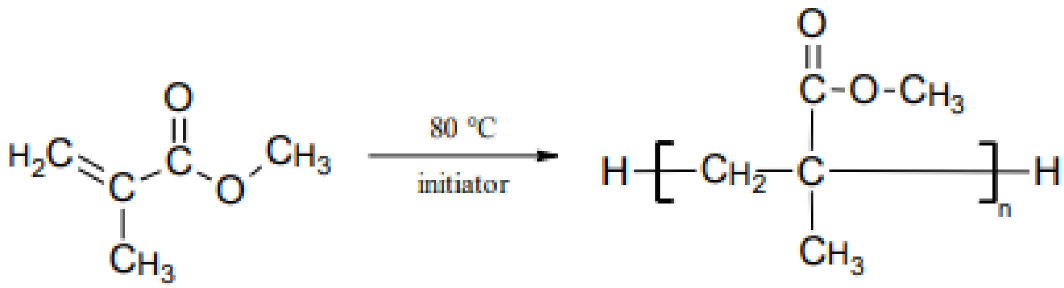

Figure 2. 5: Polymerization reaction of MMA to PMMA (Iqbal & Sun, 2018).

The formation of micelles occurs when the surfactant level is beyond its critical micelle concentration (CMC). Free radicals are produced in the aqueous phase by initiator decomposition and captured by the micelles swollen with monomer. The polymerization commences in these micelles. Compared to other polymerization processes, emulsion polymerization process will result in an increase in molecular weight of the produced latexes by decreasing the polymerization rate, either through a decrease in initiator concentration or a decrease in reaction temperature (Odian, 2004; Schild, 1992). Micelle formation polymerization has been claimed to provide chain-length control due to monomers should migrate to the inner of the droplet and react inside its borders. According to studies, the concentration of monomer and phase-transfer agent influences this process (O’toole, 1965; Bon et al., 1997).

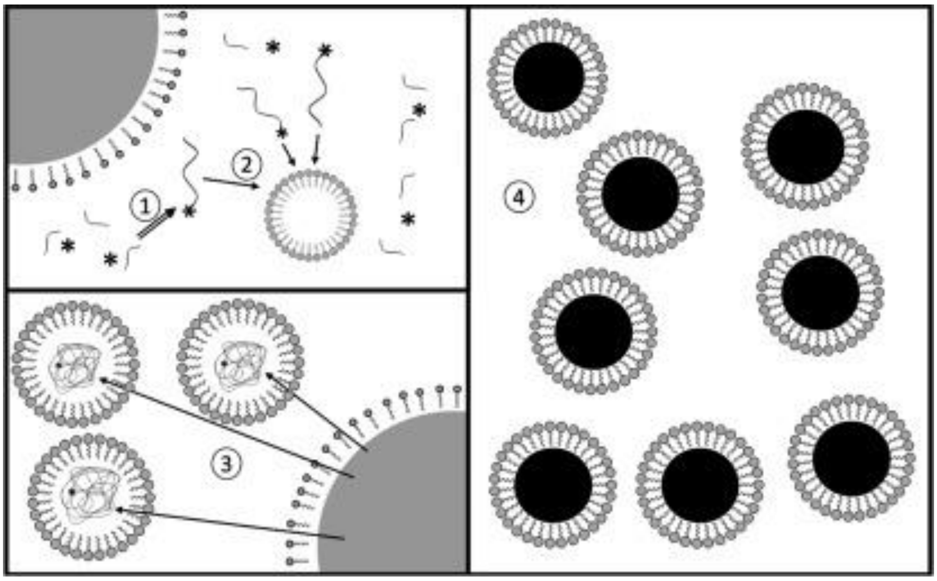

Figure 2. 6: Typical behaviour on an emulsion polymerization (Camacho-Cruz, Velazco-Medel and Bucio, 2020)

2.2.2 Role of Graphene Oxide as Polymer Nanoparticles in PPD

Recently, researchers grew more interest in producing polymeric nanoparticles by integrating nano-graphenic sheets into the polymer matrix such as PMMA for the application of transporting crude oil. Graphene oxide is one of the derivatives of graphene has received significant attention lately due to its benefits of light-weighted, having large surface areas, and low thickness which is about 1-1.4 nm (Zhang et al., 2017). It was investigated that oxidized graphene, GO have abundant number of oxygen-containing functionalities present on the surface of GO flakes, such as hydroxyl, epoxide, carbonyl, and carboxyl groups in its basal planes and around periphery, which makes it having stronger interface with PMMA and act as possible sites for polymerization (Valles et al., 2015; Kumar et al., 2016).

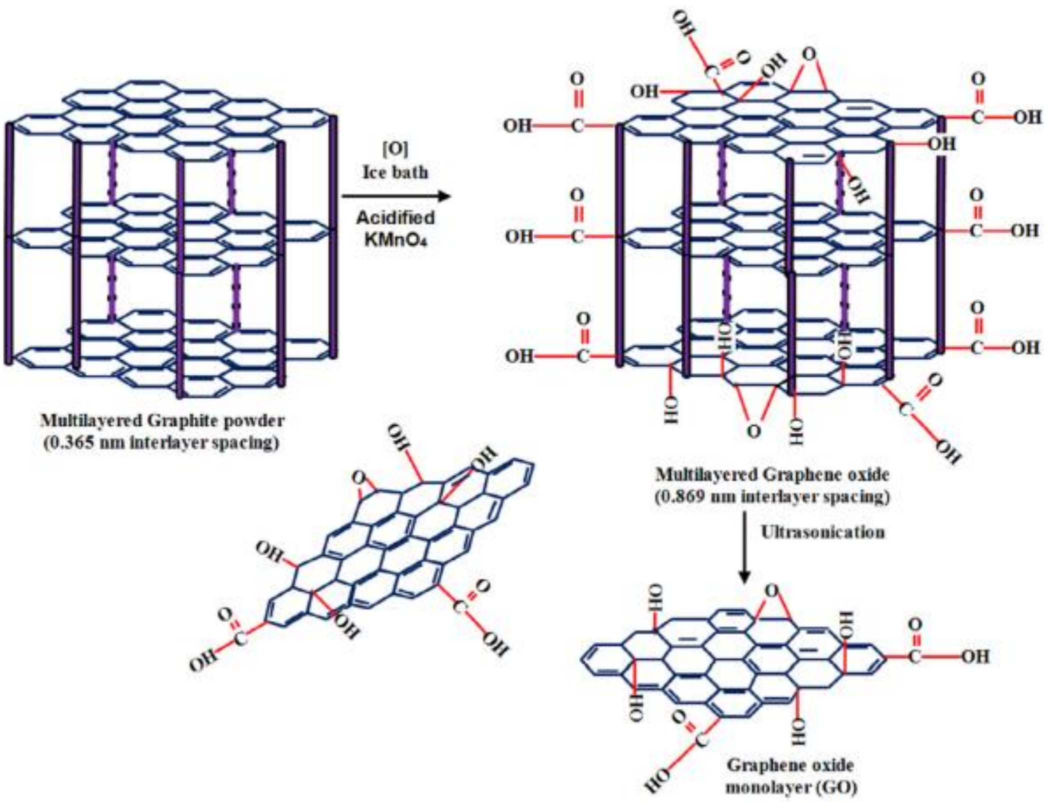

Figure 2. 7: Schematic three dimensional diagram of synthesized multi-layered graphene oxide (Sharma, Mahto, & Vuthaluru, 2019).