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Preparation and Application of Poly(methyl methacrylate)/alkyl imidazolium Modified Bentonite Nanocomposites for Deposition Mitigation of Nigerian Waxy Crude Oil

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ABSTRACT

A Nigerian montmorillonite-rich local bentonite was modified with alkyl imidazolium salts to produce organoclays and polymer/clay nanocomposites. The polymer/clay nanocomposites were evaluated for effective control of paraffin deposition in one of the NAOC (Nigerian Agip Oil Company) installations with severe paraffin deposit problems in the Niger Delta region of Nigeria. It demonstrated that efficient wax deposition mitigation (control) strategies could be developed because HTGC can be used to directly and quantitatively determine the distribution of high molecular weight components in crude oils. The results from this study illustrate the complex nature of wax inhibition. The nanocomposites tested did reduce the total amount of deposition, and nanocomposites containing 3-5wt% organic clay function better in suppressing the deposition of the high molecular weight paraffin. However, nanocomposites containing 10 – 15 % organoclay have significant success in suppressing the deposition of the low molecular weight paraffin components. Understanding the mechanism of these nanocomposite additives can lead to the development of new inhibitors that can eliminate the requirement for mechanical removal and/or extensive use of xylene-based solvents. Of the many acclaimed technology products, polymer-clay nanocomposites are among those that meet expectations. Polymer-clay nanocomposite has superior properties, compared with micro- or macro composites. For this reason, polymer-clay nanocomposites have shown a widespread presence in a variety of application areas. Polymer nanocomposites, for a variety of applications, can be created by selecting the appropriate matrix, modified organoclay, and synthetic methods. This study has demonstrated a novel polymer nano-clay application in the control of crude oil wax deposition in a Nigerian oilfield.

Keywords: *Nanocomposites, Organoclay, Crude oil, Wax, Deposition, Wax Appearance Temperature (WAT), Paraffin.*

INTRODUCTION

After the extraction of the oil from wells, it is transferred to refineries and downstream industries. One of the most common methods for transporting crude oil is pipeline transmission. The advantages of this method include the large volume of transferred oil as well as the continuous and uninterrupted oil flow. Since waxy crude oil has potential for the production of wax crystals, the design of the pipeline face high complexities due to the existence of the crystal solid phase. Flow assurance is a relatively newer term used in the oil and gas industry that refers to the flow of hydrocarbon from the reservoir to the onshore receiving facilities. Flow assurance is especially significant in the subsea oil and gas industry, which involves deep-water drilling. Hydrocarbons are obtained from subsea wells and are transferred to onshore facilities through a network of flow lines, subsea manifolds, platforms, and trunk line. Fig. 1 shows a schematic of a subsea network.

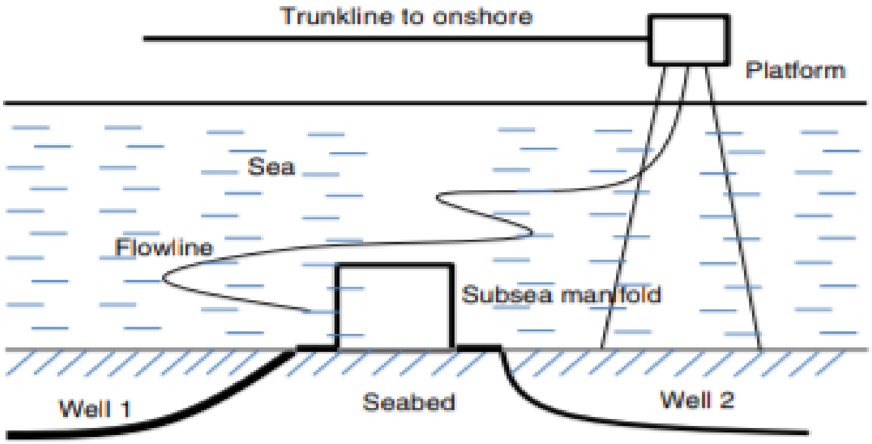

Fig. 1—Schematic of a subsea oil and gas network.

Source: Meogan White *et al.* (2018).

At large depths, high pressures and temperatures are encountered and the flow-assurance technologies aim at reducing the pressure drop between the reservoir and the onshore facilities. The pressure drop across a well transporting the hydrocarbons is a combination of the following two factors. To deal with was deposition issues, conveniently in the industry; pigging process is used for cleaning the wax after inspecting externally or cleaning as a part of regular maintenance. In the pigging process (figure 2), the deposited wax is scrapped by pass the pig devices through the pipe such that its movement along the pipe causes its head to collect the deposited layer of wax.

Mechanical removal of wax is considered as the oldest method used in the industry. This method includes the use of scrappers directly, use of scrappers in the tube, and use of “pig” device inside the pipe. Scrappers are used to scrap the tube wall and remove wax even when the well is under operation.

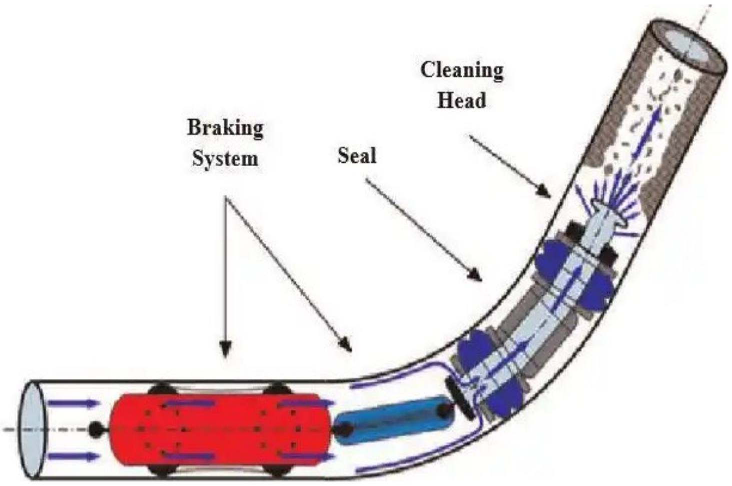

Figure 2: *Pigging process* (**Source:** Doble K, 2018)

The approaches for managing paraffin crystallization and deposition in oil fields can be broadly categorized into: (1) mechanical, (2) thermal, (3) chemical, and (4) microbial [Crake, 1954]. The mechanical method is used to remove paraffin that has been deposited inside the pore walls of tubing and other equipment (such as flow lines, pipeline, and separators) mechanically using devices known as pigs, scrappers or cutters [Al-Yaari, 2011]. A technique of high pressure water spray was proposed for wax removal using less supply of water. The use of high pressure water sprays as mechanical method, followed by injection a mixture of sterling beads to enhance erosion has been applied [Jauregui *et al*, 2009].

The chemical method is the preferred paraffin control. The chemicals used for this method includes dispersants, solvents, crystals modifiers, and surfactants. Solvents are used to dissolve paraffin deposits. Dispersants breakdown paraffin deposits into much smaller particles. Surfactants solubilize the paraffin in oil. Crystal modifiers prevent paraffin crystals from depositing by altering their growth. Crystal modifiers can also play a role I changing rheological properties such as the viscosity and pour point of crude oil [Matlach *et al.,* 1983]. These chemical methods are difficult to stabilize, because the paraffin contained in the crude oil has varying chemical composition, therefore, the chemical compatibility with target formation and reservoir conditions. Microbial methods have been used as an alternative to the conventional paraffin treatment methods as they are non-combustible, non-carcinoganic, non-pathogenic, and environmentally safe [Sakthipriya *et al*, 2017]. This method uses microorganisms to produce by-products that act as surfactants or solvents to paraddin molecules and dissolve or eliminate deposited paraffin in the formation [Etou mi, 2007]. However, microbial growth and activity can be limited by reservoir conditions such as temperature, pressure, salinity, and permeability.

The problem of wax deposition has become such a flow assurance concern that its severity must be assessed in the design of nearly subsea development across the world, including the Gulf of Mexico (Kleinhans, Niesen, & Brown, 2000), the North Slope (Ashford, Blount, Marcou, &

Ralph, 1990), the North Sea (Labes-Carrier, Ronningsen, Kolnes, & Leporcher, 2022; Ronningsen, 2012), North Africa (Barry, 1971), Northeast Asia (Ding, Zhang, Li, Zhang, & Yang, 2006; Bokin, Febrianti, Khabibullin, & Perez, 2010), Southern Asia (Agrawal, Khan, Surianarayanan, & Joshi, 1990; Suppiah *et al.,* 2010), and South America (Gracia, 2001). Significant operational hazards due to wax deposition have been reported over the past few decades. The U.S Minerals Management Service reported occurrences of wax-related pipeline plugging in the Gulf of Mexico between the years 1992 and 2002 (Zhu, Walker, & Liang, 2008). One the most severe cases was reported by Elf Aquitaine in which a removal of a wax-related pipeline blockage cost as much as $5. The remediation of this blockage resulted in a 40-day shutdown of the pipeline, which added an additional loss of $25 million of deferred revenue (Venkatesan, 2004). The arguably most notorious incidence might be from the Staffa Field, Block 3/8b, UK North sea, in which the problem of wax deposition, after several unsuccessful attempts for remediation, eventually led to the abandonment of the field and its platform (Gluyas & Underhill, 2003), leading to an estimated loss of as much as $1 billion (Singh, 2000). For long-distance pipelines where a significant portion of the pipeline is subjected to wax deposition risk, the most frequently used remediation method is called “pigging,” which uses an inspection gauge with brushes or blades on its surface to scrape off the wax deposits on the wall (Goczynski & Kempton, 2006). Normal production is usually interrupted during the pigging operations, adding operations, adding to the cost of production. The frequency of pigging can greatly influence the production cost. It should be noted that the oil price nowadays has increased and thud, the production costs related to pigging will be much higher.

The characteristics of crude oil play a significant role in its production, transport, refining, and storage. Hence, it is necessary to understand and predict the performance of waxy crude oil and their wax to avoid various problems of pipelines plugging and clogging. Several observations from industrial field have shown frequency of wax formation during production of the oil crude [Abbas, 2014]. Countries such as Kuwait, Qatar, Uganda, and South Sudan have waxy crude oil in their reserves (Siva Kumar *et al,* 2018). A drastic decrease in productivity from 30,000 Barrels of Oil Per Day (bopd) to zero within 24 h was observed in the North Sea Miller field (Gabtree *et al*, 1999). The Alba field located on the UK continental shelf and the Zakum fields located in Abu-Dhabi are included among the world’s largest oil fields where sulphate and carbonate scale were found (Strachan *et al* 2013). More information about the composition and characterization of waxy crude oils in different regions is shown in Table 1. Most of the countries exhibit a good relationship between wax content, API gravity, wax appearance temperature (WAT), and pour point (Marwa *et al*, 2019).

Waxy crude oils are found in west central Africa. Angola, Gabon, and Nigeria are examples of areas producing primarily waxy oils. Nigeria has a substantial reserve of paraffinic crude oils [Ajienka and Ikoku, 1997), known for their good quality (low sulphur, high API gravity), and containing moderate to high contents of paraffin waxes. ChevronTexaco, ExxomMobil, Total, Agip, and ConocoPhillips are the major multinationals involved in Nigeria oil sector. The main production activity in Nigeria is in the Niger Delta region, which according to master plan, extends to over an area of about 70,000 square kilometers which amounts 7.5% of Nigeria’s land mass. It lies between latitude 3^0N and 6^0N and longitude 5^0E and 8^0E (Fig 4). The

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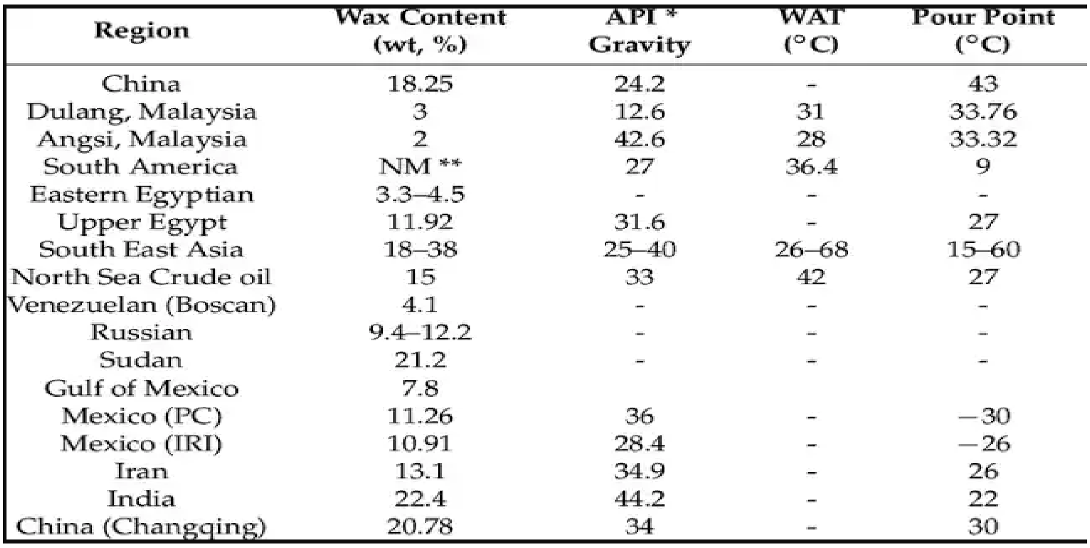
Niger Delta is world's third largest wetland after Holland and Mississippi. It covers a coastline of 560 km, which is about two-thirds of the entire coastline of Nigeria (Fawehinmi, 2007).

Table 1: Wax contents, API gravity, WAT, and pour point values of waxy crude oil from diverse regions



Region	Wax Content (wt, %)	API * Gravity	WAT (°C)	Pour Point (°C)
China	18.25	24.2	-	43
Dulang, Malaysia	3	12.6	31	33.76
Angsi, Malaysia	2	42.6	28	33.32
South America	NM **	27	36.4	9
Eastern Egyptian	3.3–4.5	-	-	-
Upper Egypt	11.92	31.6	-	27
South East Asia	18–38	25–40	26–68	15–60
North Sea Crude oil	15	33	42	27
Venezuelan (Boscan)	4.1	-	-	-
Russian	9.4–12.2	-	-	-
Sudan	21.2	-	-	-
Gulf of Mexico	7.8			
Mexico (PC)	11.26	36	-	−30
Mexico (IRI)	10.91	28.4	-	−26
Iran	13.1	34.9	-	26
India	22.4	44.2	-	22
China (Changqing)	20.78	34	-	30

*API = American Petroleum Institute, **NM = Not mentioned

Source: Adapted from: Marwa *et al*, 2019.

Fig. 3: Wax plug in wellbore on platform C in North Sea (Labes-Carrier *et al.,* 2002).

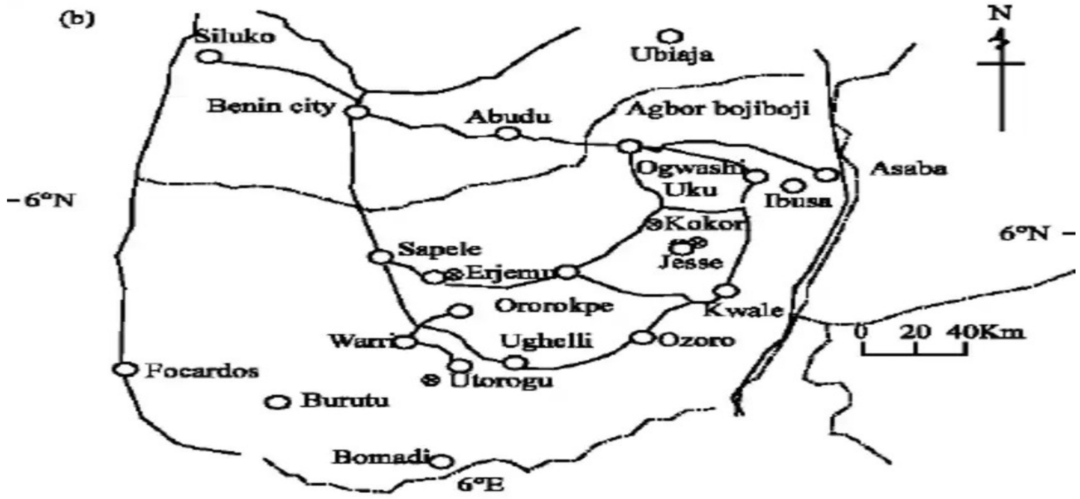


Fig. 4: Niger Delta region, Nigeria

The crude oil found in the Niger Delta region of Nigeria has wax deposits in the range of 30-45% (Adewusi 1997a). The deposition of wax in the pipes during petroleum production may cause reduced production, frequent downtime, mechanical failure of tubular equipment and ultimately, an increase in production cost (Theyab and Yahaya 2018). This has necessitated the use of many wax monitoring techniques and application of corrective measures [Toyin Olabisi Odutola and Chinenye Anita Idemili, 2020].

The accumulation of paraffin wax in petroleum reservoirs and production equipment remains a continuous problem and expenses in the production of oil. The use of scrappers, hot-oil treatments and solvent has eased the problem; however, with the advent of extremely deep production, offshore drilling and ocean floor completions, the application of remedial measures becomes prohibitive economically. As a result, use of chemical additives as paraffin deposition inhibitors is becoming more prevalent. Among the different treatments, the use of chemical inhibitors has increased in the crude oil industry as there are a number of chemicals with paraffin inhibition properties. However, there is not an inhibitor equally effective in all wells and is usual to find a chemical which performs correctly in a well but it fails in another one even in the same basin [Touller *et al.,* 2004]. Therefore, the application of chemical inhibitors is frequently restricted to each well.

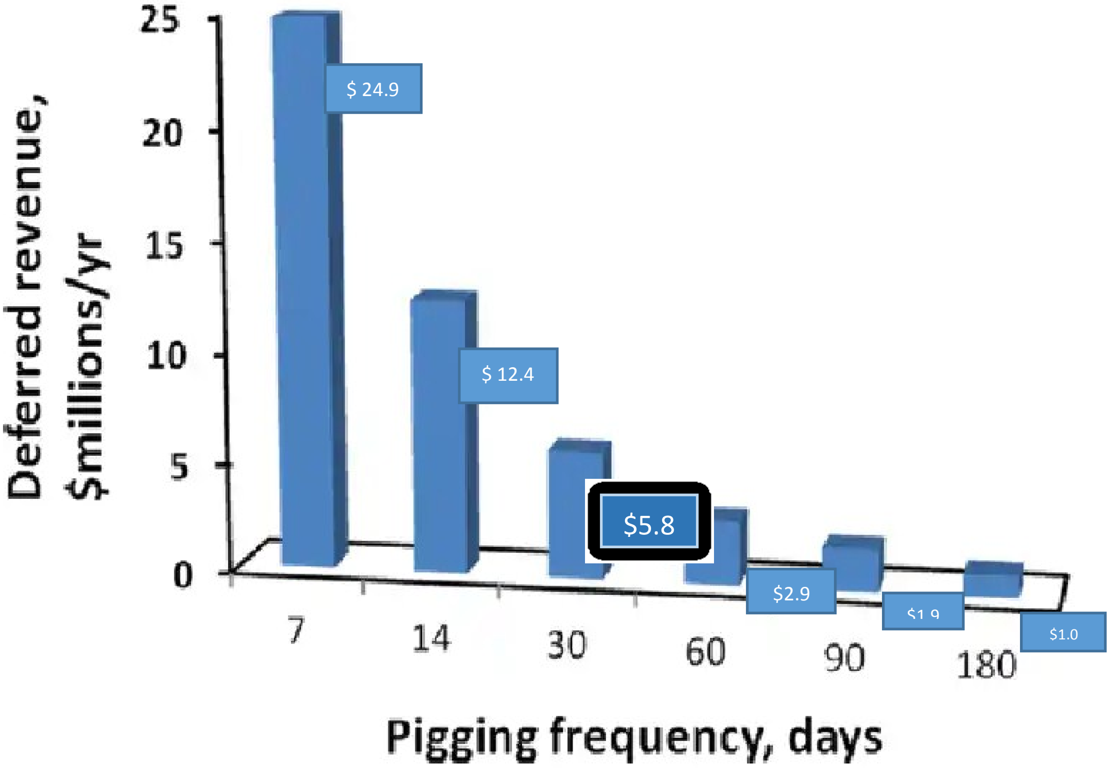


Figure 5: Cost of deferred production due to pigging estimated by Niesen (2002).

Wax inhibitors are usually grouped in three main categories:

- Wax crystal modifiers
- Detergents
- Dispersants

Detergents and dispersants are basically surface-active agents as, for example, polyesters and amine ethoxylates. They prevent or limit sedimentation of crystals by keeping them dispersed as separate particles, thus reducing their trend to interact with and to adhere to solid surface [Maithufi *et al.*, 2011). Wax crystals modifiers are chemicals capable of growing into wax crystals and alter their growth and surface properties. These chemicals reduce the affinity of crystals to interlock and form three-dimensional networks, thereby lowering the pour point and the viscosity. For that, they are commonly named pour point depressants (PPD) (Yong 1996; Pedersen, 2003). Pretreatment of crude oils with those chemicals is an attractive alternative to solve wax deposition problems during transport of crude oils along pipelines [Chen *et al.,* 2010].

The industrial PPDs have been categorized into copolymers, comb polymers and nanohybrid PPD [Yang *et al*., 2015]. Copolymers usually consist of a polyethylene (PE) backbone that contains amorphous moieties with possibly higher polarity. Such chemistries include ethylenepropylene (PE-PEP), ethylene-butene (PE-PEB), poly(maleic anhydride amide co-a-olefin) (MAC), and ethylene-vinyl actetate copolymer (EVA) [Tinsley *et al.,* 2009]. Comb polymers can be based on these, but additionally include pendant alkyl chains. Ideally, such alkyl chains should match the average carbon number of the crude oil waxes [Chen, *et al.,* 2014]. Pendant alkyl chains and polar moieties can promote polymer interactions with wax and more polar components of the crude oil, such as asphaltenes.

The pure point depressant (PPD) is effective in improving the low-temperature flowability of crude oil [Alcazar-Vara *et al.,* 2011]. It can be easily differentiated into a few categories from the perspective of its chemical structure. The first is the polymer composed of a long main chain and short side chains, for example, poly(butylacrylate), ethylene-vinyl acetate copolymer (EVA) [Kondra Sheva, 2013) etc.; the second polymer with long side chains, such as poly(maleic anhydride amide – α-olefin [Li *et al*, 2011], poly(octadecyl acrylate – maleic anhydride) etc.; and the third is the polymer including aromatic segments, such as poly(maliec anhydride – benzyl alcohol) [Wu *et al*, 2012], poly(styrene – octadecyl maleimide), etc. Apparently, all of these PPDs contain nonpolar and polar moieties, which dramatically influence the efficiency of the PPD [Cao *et al*, 2015].

The nonpolar moieties can adsorb wax molecules and cocrystallize with them [Chen *et al*, 2010], whereas the polar moieties are responsible for providing electrostatic repulsion to wax crystals and dis organizing the crystallization process of wax [Lei, 2014]. Xu *et al* [2013] synthesized with several poly(maleic alkylamide –α-octadencene) copolymers with different contents of carboxyl group, and found that moieties could alter the shape of the wax crystal and prevent the wax from forming a layer structure. Erceg Kuzmic et al, also revealed that the carboxyl group and heterocyclic nitrogen of the PPD could change the size of the wax crystal and reduce the gel strength of crude oil. The PPDs have quite strong selectivity to crude oil, and a kind of PPD is hard to be efficient for all waxy crude oils. But EVA has been widely used as the PPD for many kinds of crude oils [Machado *et al*, 2002]. The ethylene chain of EVA can recrystallize with waxes, whereas the vinyl acetate of that can provide electrostatic repulsion force to wax crystals [Jafari *et al*, 2013]. In addition, the efficacy of EVA was largely dependent on its content of polar groups. It also had been reported that EVA with modified polar groups performed better than untreated EVA [Yongwen *et al*, 2022]. However, the influence of modified poplar groups of EVA on the crystallization process of wax and the low-temperature flowability of crude is seldom reported systematically. PPDs function by co-crystallizing into the paraffin structure via van der Waals forces. This allows the polar end tail (unattached) to form a steric interference with the alignment of other new wax molecules. PPDs decrease the pour point temperatures of the crude oil and then weaken the wax deposition solid structure, thus allowing for the easy removal of the deposition by shear force.

Another type of PPD that is commonly used in the industry is the comb polymer, which can be categorized into two different polymer groups: maleic anhydride copolymer (MAC) and poly-acrylate/methacrylate (PA or PMA) ester polymers. The length of the pendant chain as well as the length of the chain wax should be similar to obtain optimum deposition inhibition performance. Some details about wax inhibitors and PPDs are summarized in tables. Due to challenges in dealing with waxy crude oil, theses polymeric PPDs showed limited wax inhibition performance. Recent findings showed that nanotechnology had contributed in the development of wax deposition inhibitors. Nanoparticles and nanoparticle-polymer composites have been subject to recent studies, due to their ability to improve pour point beneficiation [Yao *et al* 2016, Norman *et al* 2016 Zhao *et al* 2018]. Such particles were stated to function as wax nucleation sites, which can lead to the formation of larger aggregates that are more compact and more amorphous in structure [Zhang *et al*, 1999, Ruwoldt *et al* 2018].

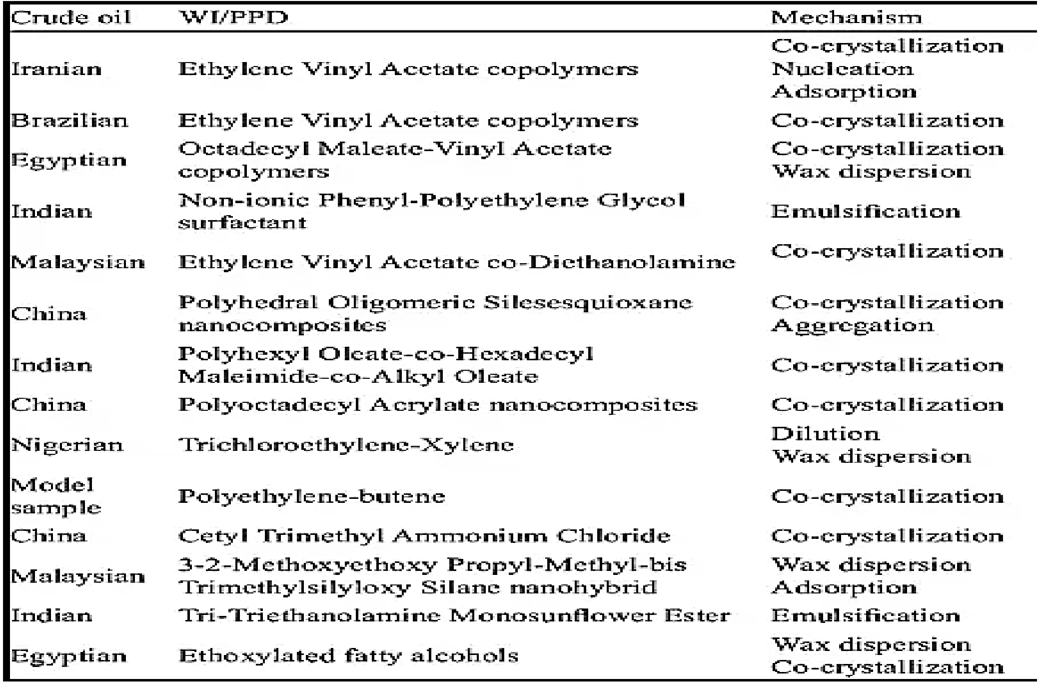
Table 2: Efficiency of the various polymeric additives

EVA	Concentration	Sample oil	Pour point reduction	Viscosity reduction (%)
EVA	500 ppm, 4^{0}C	Albacore 2, Brazil	>2	N/A
			>2	N/A
			>2	N/A
EVA-co-diethanolamine	1 g EVA+5ml DEA, 4^{0}C	Malaysian crude oil	5	7.53
EVA with modified montmorillonite	100 ppm, 30^{0}C	Jinqiao pipeline company, Xuzhao, China	9	82.1
EVA copolymer with polymethylsilsesquioxane	50 ppm EVA + 2.5 ppm PMSQ, 24^{0}C	Qinhai waxy crude oil	18	45.78
n-alkane acrylates-co-n-hexadecylmaleimide	1000 ppm, 24^{0}C	Nada crude oi, Gujerat, India	27	87.88
Polyoalkyl acrylate contained ammonium	wt% 15^{0}C	Verkhne-Salatskoye Urmanskoye	1.6	22.39
	0.05 wt%, 15^{0}C		7.5	87.69
Polyoctadecyacrylate	800 mg/kg POA/clay, 5^{0}C	Changqing China	9	33.75
Polymethacrylate	500 ppm, 50^{0}C	Jinghe, China	5.4	9.9
			3.2	30.7
Polystyrene-maleic anhydride	10000 ppm, 27^{0}C	N/A	30	78.18
Maleic anhydride copolymers with alkyl linoleate or tetraesters	5000 ppm, 15^0 3000 ppm, 15^{0}C	Alamin, Egypt	18	77.03
Maleic anhydride-co-Octadene	3000 ppm, 9^{0}C	Norpetco, Egypt	24	97.78
			18	96.05
Modified maleic anhydride copolymer	500 ppm, 26^{0}C	Changqing crude oil	9	N/A
			12	N/A
			13	N/A
			19	88.4
Cyclohexanone pentaerythritol ketal	500-1000 mg/L, 20^{0}C	Jinghe, China	2.7	58.06
		Xinjiang, China	2.4	42.05
Poly(hexyl oleate-co-hexadecyl maleimide-co-n-alkyl oleate)	1000 ppm, 16^{0}C	Langhnaj, India	3	54.55
			6	67.68
			6	56.23

α–olefin styrene	2000 ppm, 60^{0}C	Western Desert, Egypt	21	N/A

Source: SM Anisuzzaman *et al*, 2018.

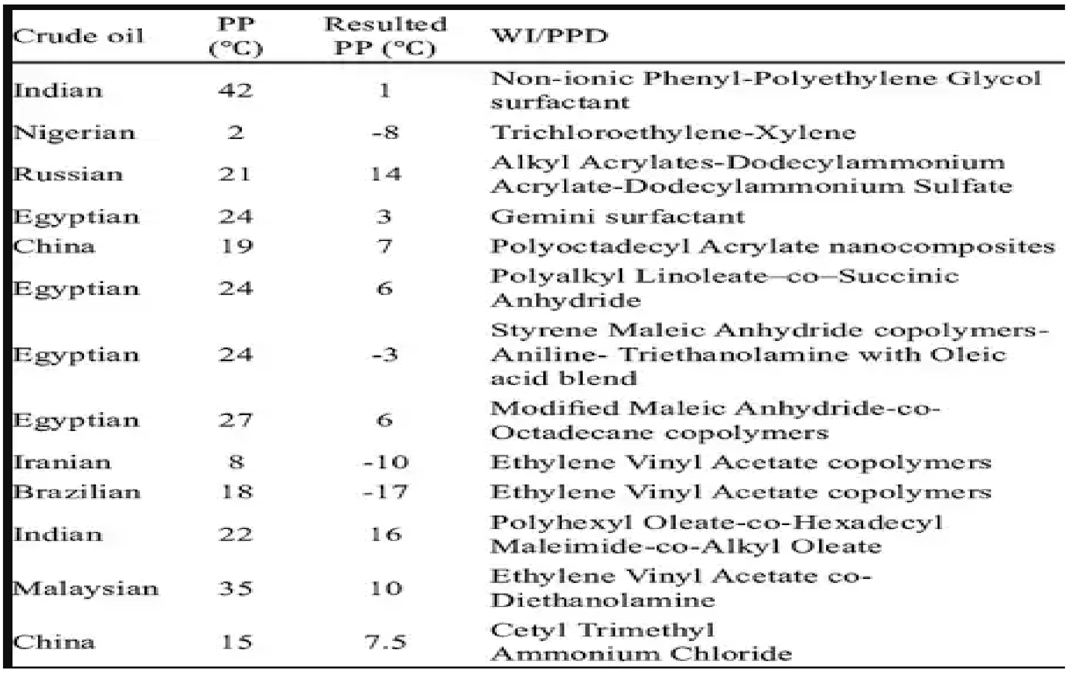
Table 3: Wax inhibitors and pour point depressants and their corresponding mechanisms



Crude oil	WI/PPD	Mechanism
Iranian	Ethylene Vinyl Acetate copolymers	Co-crystallization Nucleation Adsorption
Brazilian	Ethylene Vinyl Acetate copolymers	Co-crystallization
Egyptian	Octadecyl Maleate-Vinyl Acetate copolymers	Co-crystallization Wax dispersion
Indian	Non-ionic Phenyl-Polyethylene Glycol surfactant	Emulsification
Malaysian	Ethylene Vinyl Acetate co-Diethanolamine	Co-crystallization
China	Polyhedral Oligomeric Silesesquioxane nanocomposites	Co-crystallization Aggregation
Indian	Polyhexyl Oleate-co-Hexadecyl Maleimide-co-Alkyl Oleate	Co-crystallization
China	Polyoctadecyl Acrylate nanocomposites	Co-crystallization
Nigerian	Trichloroethylene-Xylene	Dilution Wax dispersion
Model sample	Polyethylene-butene	Co-crystallization
China	Cetyl Trimethyl Ammonium Chloride	Co-crystallization
Malaysian	3-2-Methoxyethoxy Propyl-Methyl-bis Trimethylsilyloxy Silane nanohybrid	Wax dispersion Adsorption
Indian	Tri-Triethanolamine Monosunflower Ester	Emulsification
Egyptian	Ethoxylated fatty alcohols	Wax dispersion Co-crystallization

Source: Taken from; Lim Zhen Hao, *et al,* 2019

Table 4: Reduction of pour point using different wax inhibitors and pour point depressants



Crude oil	PP (°C)	Resulted PP (°C)	WI/PPD
Indian	42	1	Non-ionic Phenyl-Polyethylene Glycol surfactant
Nigerian	2	-8	Trichloroethylene-Xylene
Russian	21	14	Alkyl Acrylates-Dodecylammonium Acrylate-Dodecylammonium Sulfate
Egyptian	24	3	Gemini surfactant
China	19	7	Polyoctadecyl Acrylate nanocomposites
Egyptian	24	6	Polyalkyl Linoleate–co–Succinic Anhydride
Egyptian	24	-3	Styrene Maleic Anhydride copolymers-Aniline- Triethanolamine with Oleic acid blend
Egyptian	27	6	Modified Maleic Anhydride-co-Octadecane copolymers
Iranian	8	-10	Ethylene Vinyl Acetate copolymers
Brazilian	18	-17	Ethylene Vinyl Acetate copolymers
Indian	22	16	Polyhexyl Oleate-co-Hexadecyl Maleimide-co-Alkyl Oleate
Malaysian	35	10	Ethylene Vinyl Acetate co-Diethanolamine
China	15	7.5	Cetyl Trimethyl Ammonium Chloride

Source: Adapted from: Lim Zhen Hao, *et al,* 2019

A new generation of PPDs based on nanotechnology, including nanocomposites, has attracted much attention in recent years. Nano-silica and modified montmorillonite nano-clay have been very populated in recent studies [Kazemi *et al* 2002]. Montmorillonite is a type of clay that is widely found in bentonite rocks with the chemical formular $(Na, Ca)(Al, Mg)_6 (Si_4O_{10})_3 (OH)_6$-$nH_2O$ (Hydrated Sodium Calcium Aluminum-Magnesium Silicate Hydroxide) [Fisli and Yusuf 2007]. See the advantages of PPD EVA and MMT in reducing pour point and viscosity values of crude oil, with high pour point and viscosity values. We will compare the two performances of the PPD to increase the effectiveness of the production [Nurfajrin, *et al,* 2021].

Recently, nanohybrid materials have been developed as a new type of PPD for the petroleum industry [Guolin Jing, *et al* 2017], these materials can effectively reduce the pour point and viscosity of crude oil. Zhang *et al* (1995, 1999) prepared a nanohybrid PPD with a long effect time, which can improve the anti-reheating and anti-shearing properties of the PPD. Yang *et al* (2015, 2016), prepared a poly(octadecyl acrytlate) (POA)/nanosilica hybrid PPD can provide spherical templates for wax precipitation and cause wax suppresses gelation and improves the followability of the mode waxy oil by several orders of magnitude. Notably, the POA coverage on the surface of the nanoparticles is an important factor affecting the performance properties of hybrid PPDs [Norrman *et al.*, 2016]. Nanoparticles with a low POA coverage exhibited almost no effect on the strength of the formed wax gel, whereas nanoparticles with full POA coverage substantially lowered the wax gel strength; in addition, nanoparticles with more than full POA coverage further lowered the strength of the formed wax gel. The wax appearance temperature was also lowered by the nanoparticles, and using nanoparticles with greater than 100% POA coverage resulted in a limited or no additional effect [Goulin Jing, *et al*, 2017].

Nanohybrid PPD has also been confirmed to minimize the wax deposits produced, decrease the WAT, and remove wax accumulation chances as nanoparticle have greater steadiness, good adsorption, and good capacity for diffusion (Yang et al. 2015). In addition, the nanoparticle cost is smaller than most of the polymers used, so it is further economical and inexpensive (Goulin *et al.* 2017). The use of nanoparticles has also proved practical because it offers a broader surface area that improves particle interaction with crude oil (Fakoya and Shah 2017). With the continuous development of nan-technology in recent years, nano-materials have been widely applied in industry [Zhicheng Zhao *et al.* 2016].

Polymer/inorganic nanocomposites or nano-hybrid materials have attracted attention in scientific research, especially polymer/inorganic nanocomposites, which are composed of inorganic nanoparticles in polymer matrix. These nanocomposites are formed by little dispersion of organic particles into a polymer matrix. The most heavily used filler material is based on the smectite class of aluminum silicate clays, of which the most common representative is montmorillonite (MMT). MMT has been employed in many PLS nanocomposites systems because it has a potentially high-aspect ratio and high-surface area that could lead to materials which could possibly exhibit great property enhancements. In addition, it is environmentally friendly, naturally occurring, and readily available in large quantities. Layered silicates in their pristine state are hydrophilic. Most of the engineering polymers are hydrophobic. Therefore, dispersion of native clays in most polymers is not easily achieved due to the intrinsic incompatibility of hydrophilic-layered silicates and hydrophobic engineering polymers [Ngugen and Baird, 2016].

To have successful development of clay-based nanocomposites, it is necessary to chemically modify natural clay so that it can be compatible with a chosen polymer matrix. Generally, this can be done through ion-exchange reactions that replace interlayer cations with quarternary alkylalmmonium or alkylphosphonium cations. It is well established that when layered silicates are uniformly dispersed (exfoliated) in a polymer matrix, the composite properties can be improved to a dramatic extent [Nguyen and Baird, 2006].

The limited thermal sability of alkylammonium cations intercalated into smectite minerals (e.g., montmorrillonite, MMT) and the processing instability of some polymers in the presemce of nanodispersed MMT have motivated the development of improved organphilic treatments for layered silicates. Polymer/clay nanocomposites show great promise for materials science applications, but the synthesis and successful development of these materials is not simple. Careful selection and consideration of the entire nanocomposite system must be undertaken before a successful polymer-clay nanocomposite (or any nanocomposite for that matter) can be prepared and utilized for a new materials science application. If the wrong organoclay is chosen for a particular polymer, the nanocomposite may never be formed, as the nanoparticles might nit disperse well enough. Further, even if the best organoclay is chosen, poor mixing or synthetic processes can result in a material with properties worse than the starting polymer. Finally, the target application will dictate clay loading, or whether clay is even acceptable for that final application [Morgan, 2022].

Polymer/clay nanocomposites are materials that display rather unique properties, even at low clay content, by comparison with more conventional mineral-filled polymers. Nanocomposites have a number of advantages over traditional polymer composites. Conventional composites usually require a high content (>10 wt%) of the inorganic filler to impart the desired properties. Such high filler levels increase the density of the product and can cause deterioration in properties through interfacial incompatibility between the filler and the organic matrix [Amirhossein Esfandiari *et al,* 2008].

Problem Statement and Project objective

Crude oils originating from the Niger Deltaregion of Nigeria have attracted significant attention in the last two decades because these oils have relatively low amount of sulfur and heavy metals, making the refining processes much easier. However, the oils are paraffinic which leads to some problems with their transportation and storage. The Nigerian Niger Delta crude oil, which is the mainstay of Nigerian economy, exhibits waxiness, with deposits in the range of 30-45% [Adewusi, 1997b]; [Fasesan & Adesumi, 2003]; [Taiwo, 2009]; [Oladipo, 2009]. Production tubing has also been known to wax up, necessitating frequent wax cutting, using scrapers conveyed by wire lines, which is an expensive practice. Billions of dollars have been lost to its prevention and remediation [Oladipo, 2009]. The resultant effect on the petroleum industries include among others, reduced or deferred production, well shut-in, pipeline replacements and/or abandonment. For efficient operation of a pipeline system, steady and continuous flow without any interruption is desirable [Chang, 1999].

Although wax deposition is a commonly encountered problem in production operations, there is no universally effective treatment for the problem. Treatment methods are usually highly case-dependent, requiring the proper identification of the mechanisms for deposition and the development of a technique that is specific for the target field. A properly designed and implemented chemical method for preventing wax deposition is essential for cost-effective production in the unique environment of the Niger-Delta region.

EXPERIMENTAL SECTION

Material

Bentonite clay samples from deposits in Nigeria have been observed to contain impunities in its raw for hence the need for beneficiation (James *et al.,* 2008; Obaje, 2012). Estimation of the Nigerian bentonite reserve has been spearheaded by the Raw Materials Research Development Council (RMRDC) which is a research parastatal of the Federal Government of Nigeria. Beneficiation was done using sodium salt such as sodium carbonate (Na_2CO_3) or sodium hydrogen carbonate ($NaHCO_3$) which allowed for the conversion of the mainly calcium montmorrilonite clays to sodium montrillonite via an ion exchange mechanism. Alkyl bromide or chloride, 1, 2-dimethyl imidazole, and other organic chemicals for the synthesis of imidazolium salts were purchased from Sigma-Aldrich (Germany) and Acros (Belgium) companies. 1-Dodecyl-3-methylimidazolium bromide (C_{12}mimBr) and C12mimPF_6 were supplied by Lanzhou Institute of Chemical Physics, Chinese Academy of Science. PMMA was obtained from Aldrich Chemical Company with a number-average molar mass of 57 100g mol^{-1} and a dispersity ($D = M_w/M_n$) of 1.97.

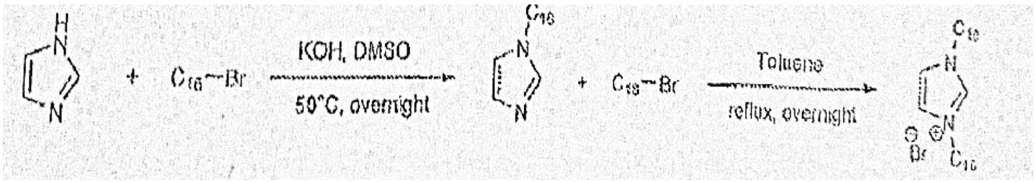
Preparation of imidazolium modified Montmonilonites (bentonite clay).
The preparation of the modified clays was performed in two steps. The first step of the preparation of modified clays was the synthesis of the imidazolium salt. The second step was the exchange of the imidazolium in the clay. The procrdures for the synthesis of the imadzolium salts were adapted from the following references with slight modifications:

1) Gilman J.W., Awad W.H., Davis R.D., Delong H.C. Chem Mater (2002) 14, 3776;
2) Awad W.H., Gilman J.W., Nyden M., Harris R.H., Sutto T.E., Callahan J., Trulove P.C., Delong H.C., Fox D.M and Thermochimica Acta, 409(1), 3-11 (2004) and
3) J. Langat, S. Bellayer, P. Hudrlik, A. Hudrlik, P.H. Maupin, J.W Gilman Sr, D. Raghavan, Polymer 47 (2006) 6698-6709

Preparation and Characterization of Alkyl-Imidazolium Salts

A round bottom flask equipped with a reflux condensor was chaeged with alkyl bromide or chloride (1 mole), 1-2dimethyl imidazole (distilled, 0.95 mole) and acetonitrile (50 mL). The solution was agitated and refluxed for 7 to 10 d in a nitrogen atmosphere. The crude product was filtered then redissolved and reprecipitated several times using acetonitrile (solvent) and ethyl acetate (non-solvent); excess solvent was removed at high vacuum (12 h at $80^0 \pm 5^0$C). The 1-alkyl-2,3-dimethylimidazolium bromide or chloride salt was a white precipate. Typical yield was 60% - 80%. Non-halide counter amions, such as BF_4^-, PF_6^-, were synthesized via ion exchange using an excess of the ammonium salt, such as NH_4PF_6.

The N,N-dialkyl imidazole chloride salts utilized in the present work was synthesized by the procedure illustrated below:



The synthesis procedure is described in more detail in Starikova, Dolgushin, Larina, Komarova and ARKIVOC (Gainesville, FL, United States) (2003), (13), 119-124

General procedure for preparing 1,3-Dialkylazolium halides: Alkyl bromide (0.105 mol), was added drop wise under vigorous stirring to a mixture of 0.1 mol of 1-alkylimadzole or 1-alkylbenzimidazole in 200 ml of anhydrous toluene. The mixture stirred overnight at reflux temperature, and the solvent was distilled off. The residue was washed 4 times with THF, the suspension was filtered out and dried in an oven under reduced pressure. The products were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, and thermal gravimetric analysis (TGA).

Preparation and Characterization of Alkyl Imidazolium modified Montmorillonite (Oragnoclay)

The preparation of the organoclay was conducted using two routes. In the first route, the preparation of alkyl-imidazolium montmorillonite consisted of a cation-exchange reaction between the montmorillonite-layer silicate and excess of alkyl-imidazolium salt (40% in respect of the exchange capacity of the host). The salt was dissolved in methanol at 60^0C, and then was added drop wise at an aqueous suspension of montmorillonite (1 wt.%). The mixture was stirred for 5h at 60^0C at room temperature overnight. The imidazolium-exchange montmorillinite was collected by filtration and washed with 1 liter of deionized water (10 x 100 ml) to remove all residual anions. The product was then dried at room temperature and then under vacuum at 100^0C overnight, pulverized and purified 5 times with dichloromethane. The characterization of the modified clay was carried out by TGA and XRD analysis.

In the second route, a beaker was charges with an aqueous MMT slurry (30g, 3% by mass of clay) that was heated to 60^0C ± 5^0C while agitating. To the preheated slurry was added at 60^0C ± 5^0C aqueous imidazollium slurry (3% by mass of imidazolium salt, 1.1 eq of imidazolium salt with respect to clay CEC value). The mixture was agitated overnight at 60^0C ± 5^0C using a magnetic stirrer and was filtered and washed with a large excess of deionized water. The yellowish crude product was air-dried, ground to a fine powder using a mortar and pestle, and was soxhlet extracted with ethanol for 24h in a convection oven, while still in the thimble until hard, it was ground to a fine powder and dried under high vacuum (80^0C ± 5^0C) overnight.

Instructional:

- The thermogravimetric analysis (TGA) was performed using a Perkin-Elmer TGA7 thermobalance under nitrogen atmosphere (gas flow 40ml/min) at 10^0/min heating rate from 40^0C to 900^0C.
- The wide Angle X-ray Scattering (WAXS) data were collected with an X'PertPro diffractmeter, equipped with a copper anode (K_α radiation, $\lambda = 1.5418$ A). The data were collected in the 2θ range $5^0 – 60^0$ by means of an X'Celerator detector.

Preparation and Characterization of PMMA/organoclay nanocomposites

The primary focus of this work is to develop a process for increasing the exfoliation and dispersion of nanoparticles into polymeric matrices using supercritical carbon dioxide. However, the greatest interest has involved melt processing because this is generally considered more economical, more flexible for formulation, and involves compounding and fabrication facilities commonly used in commercial practice. For most purposes, complete exfoliation of the clay platelets. i.e., separation of platelets from one another and dispersed individually in the polymer matrix, is the desired goal of the formation process [Robeson, 2008].

Part of the experiment was on melt blending of polymer/layered silicate (PLS) nanocomposite. Melt blending is the most commonly used method because of its efficiency operability, and environmental containment. In the present study, series of PMMA nanocomposites was fabricated by loading 3, 5 and 7% by weight of organoclay in the PMMA matrix. The influence of organoclay content on the properties was investigated using XRD, TEM, ETIR, TGA and DSC analysis.

To develop well-dispersed PMMA nanocomposites successfully, the metered CO_2 injection system was attached to the twin screw extruder system, which had a cylinder, syringe pump and a back pressure regulator. A schematic diagram of the experimental apparatus and detailed screw configuration are shown in Fig-6. The barrel and die temperatures were varied from 190 to 200^0C. The feed rate and the screw speed were 11.4g/min and 100-pm, respectively 100 bar. The syringe pump was set to have a constant CO_2 gas flow rate and the back pressure regulator was used to maintain constant pressure.

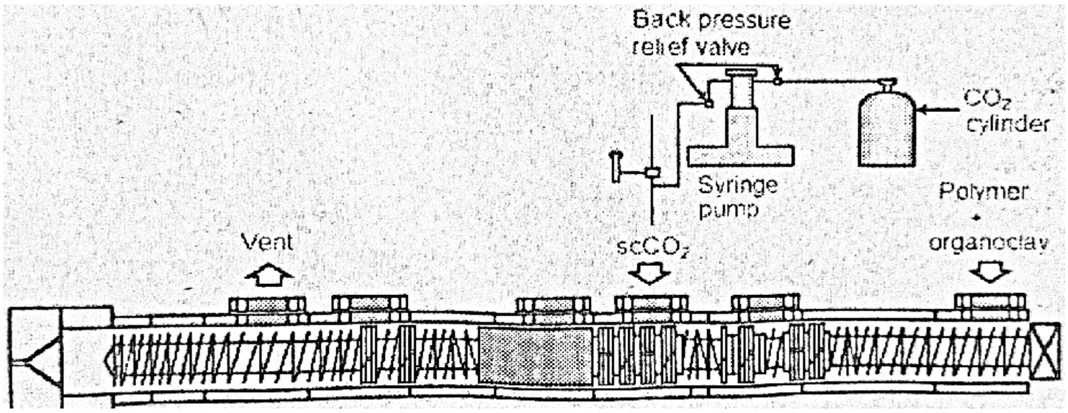


Fig 6: Twin screw extraction with $scCO_2$ and its screw configuration.

The layer surface organophilic and improves the compatibility with polymer (PMMA). The organoclays used to form the nanocomposites were studied.

Thermal Behavior: Differential scanning calorimetric studies for thermal characterization were performed on a DSC (DSC-2910, TA Instruments) at a heating rate of 10^0C/min from 30^0C to 300^0C. Thermal gravitational analysis was also conducted employing a TGA (TGA-2950, TA Instruments) to verify the thermal stability of the blends. The chamber was flushed with nitrogen. Samples of about 6mg were heated from 30 to 600^0C at a heating rate of 20^0C/min.

Electron microscopy (SEM and TEM) Morphology

SEM was used to understand the morphology of organo-clay before and after *$scCO_2$* processing. Images were collected using a Hitachi S-2400 scanning electron microscope with an electron potential of 25kV. Many (10-20) images were collected for all samples to ensure accurate representation of the clay structure. *Transmission electron microscopy* (TEM) was used to investigate the clay structure in the PMMA matrix. Thin-films of the nanocomposites were prepared by a compression molding technique. The films were cut into pieces and placed between Teflon sheets at 80^0C and compressed to form thinner films. This process was repeated to achieve a film thickness that would allow for imaging. The films were removed using liquid nitrogen and placed on 200 mesh examined with a JEOL FastEM 2010 HR TEM operated at 200kV.

Wide-angle X-ray diffraction (WAXD)

WAXD was used to determine the inter-gallery spacing of the as-received clays, $scCO_2$ processed clays, and clay/polymer nanocomposites. The d_{001} spacing for the clays was determined using the JADE software accompanying the diffractometer. The inter-gallery spacing was calculated by subtracting 1 nm (platelet thickness) from the d_{001} spacing. All data were collected using a Rigaku Rotaflex powder differactometer with a Cu Kα X-ray source ($\lambda = 1.54$ Å) and an accelerating voltage of 40 kV at a current of 150 mA. To perform scans, samples were placed in a custom made zero background quartz sample-holder that is 0.9 mm in depth. Scans were carried out in different orientations of a sample and verified to be reproducible when diffraction patterns were superimposed on one another.

Crude Oil Characterization

Samples of Crude Oil were provided by the Nigerian National Petroleum Corporation (NNPC) Port Harcourt and Warri refineries. The Department of Petroleum Resources (DPR) also assisted in oil sample collection.

Crude Oil Composition

Crude oil is composed of saturates, aromatics, resins, and asphaltenes (SARA), the distribution of which in a particular crude oil system is shown by the SARA analysis. SARA determines the susceptibility of the crude to deposition of wax solids, and thus the stability of the crude oil. Saturates are flexible in nature, the flexibility being highest in normal paraffins because they are straight chain compounds. The very flexibility of normal paraffins makes it porssible for them to easily cluster and crystalize. The iso-paraffins equally enjoy a high level of flexibility, but form a more unstable wax. Cyclo-paraffins (napthenes) are least flexible due to their cyclic nature and do not contribute much to wax deposition. These components are in thermodynamic equilibrium at initial reservoir conditions. It is known that aromatics serve as solvents for high molecular weight saturates, which are the sources of paraffin waxes in crude oil while the polar components, especially asphaltenes, induce wax nucleation (Hammami *et al*., 1999, Tao Zhu *et al.,* 2008). Oils containing high C_{30+} (especially normal paraffin C_{30+}) concentrations exhibit high cloud point temperatures (Ferworn *et al.,* 1997). Therefore, knowledge of the oil composition (SARA) gives a fair idea of the wax deposit potential of the crude and, hence, the oil stability. Oil stability has been reported to depend on its solid content and the balance between aromatics and saturates. By SARA anaylysis, the distribution by weight percent of saturates, aromatics, resins, and asphaltene components, for stable and unstable crude oil, are as follows [Tao Zhu *et al,* 2008].

Unstable crude: Saturates>Aromatics>Resins>Asphaltenes
Stable crude: Aromatics>Saturates>Resins>Asphaltenes

This distribution is to be expected since the aromatics keep the heavy paraffin wax in solution, while a crude oil system that displays a large amount of saturates (paraffin) is likely to be unstable (Carbognani *et al*., 1999) and thus precipitate and deposit wax [Toa Zhu, *et al,* 2008]. Petroleum colloids (waxes, resins, and asphaltenes) can be separated by elution process on an activated silica gel column. Figure 7 shows the sequential elution chromatography setup for separating petroleum colloids into asphaltenes (a), resins (b), and waxes (c), respectively [El-Dalatony *et al*., 2019].

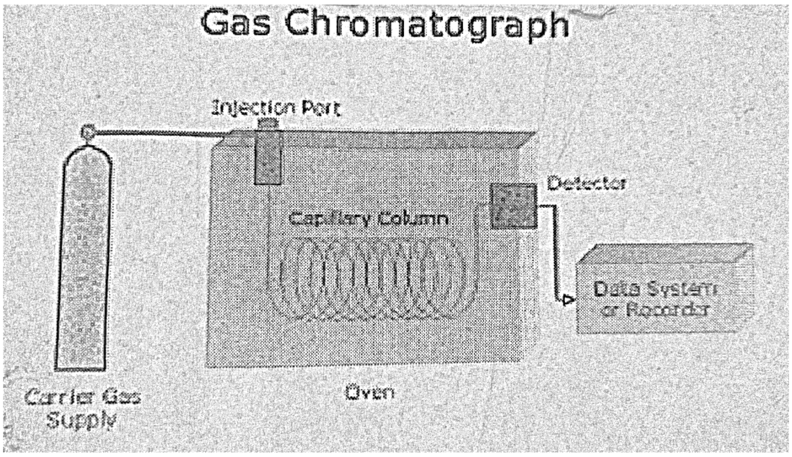


Figure 7: GC schematic A modified ASTM D2549-02 9 (elution chromatography) method was used to obtain the Saturates, Aromatics, Resins, and Asphaltene (SARA) fraction in the work.

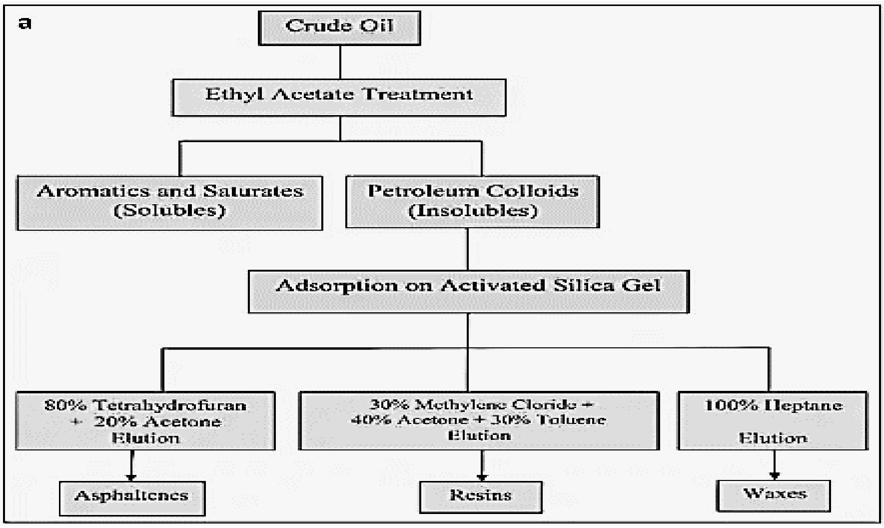


Figure 8: Sequential chromatography setup for separating petroleum colloids into waxes, resins, and asphaltenes.

SARA separation and characterization: The two oil samples were decanted and treated with n-heptane in the ratio of 1:40 as per ASTM D2007-80 standard procedure for separating asphaltene and maltene. Asphaltene and maltene were separated using filtration through a 0.45 µm filter paper. The filter paper was dried and weighed to determine the percentage of asphatene. The maltenes were fractioned into saturates, aromatics and resins by eluting with n-hexane, toluene, and choloroform, respectively, using column chromatography with activated silica gel (100-200 mesh) [Anto *et al*, 2020].

Composition Analysis

Many techniques have been developed to quantify the composition of crude oil, but by far the most utilized methods is by GC (Gas Chromatography). A complete characterization up to carbon number C_{100} can be completed in about one hour. Detection levels of ppb (parts per billion) can be repeatedly obtained with small sample size. Modern equipment has become modular and can easily be modified to perform many different analyses. Figure 2.9 depicts a basic gas chromatographer setup. The inlet, chromatographic column, and the detectors can be changed to suit the analysis. The basis behind chromatographic analysis is to separate the fluid into pure components for quantification. Separation occurs in the column where travel time is determined by boiling point and molecular size.

Hydrocarbons are eluted from a non-polar column in boiling point order (Eggerton, 1960). Branched and straight hydrocarbons with the same carbon number will elute from the column before the next incremental hydrocarbons. Columns are chosen based in the analysis to be performed. Out of the many possible detectors, the FID (lame ionization detector) and the TCD (thermal conductivity detector) are the most common. The FID burns hydrogen with air to produce a base signal. When analyte passes through the flame, the signal increases and is recorded in the detector. The limitation with this type of detector is that it will not detect nitrogen, carbon dioxide, or anything else that will not burn. Sensitivity is excellent and has the possibility to detect ppt (parts per trillion) if the sample is carefully prepared.

Wax Appearance Temperature: The wax appearance temperature was determined by Differential Scanning Calorimetry (DSC) according to the standard test method ASTM D4419. For the measurements a sample of 10 – 15 milligrams was weighed and sealed in a pan with hermetic lids. The temperature program includes a heating cycle up to 80^0C to erase the thermal history of the sample, followed by a cooling sample from 80^0C to -30^0C at a rate of 10^0C/min. A second heating cycle was acquired from -30^0C to 80^0C. The wax appearance temperature (WAT) and wax disappearance temperature were obtained from the cooling and heating cycles, respectively, from the onset of the exothermic and endothermic peaks in the corresponding thermograms.

In another experiment, the DSC analysis of the oil samples was carried out using a DSC apparatus (Mattler-Toledo DSC822e, Switzerland). In each measurement, 6-8 mg oil sample was placed in the pans of DSC and then the sample was heated (at a rate of 11^0C/min) from room temperature to 50^0C in the N2 environment (with a flow rate of 20 mL/min). At 50^0C, the sample was kept for 5 min to remove the effect of memory effect of wax formation. Then the sample was cooled from 50^0C to -20^0C at a rate of 8^0C/min. During the cooling stage, the change in the heat was recorded.

Microscope observation of the morphology of wax crystals

The saturates of the waxy crude oil extracted and placed on the glass slide of a polarized microscopy (BX41-P OLYMPUS, Japan) to observe the process of formation and morphology of the wax crystals. Before each test, the saturates sample was heated to 50^0C to melt the already formed wax crystals. Then the sample was cooled from 50^0C to 10^0C to facilitate the formation of the wax crystals. During the observation, the temperature of the copper stage placed on the microscopy was kept at 10^0C.

In another experiment, the procedure developed by Jost Ruwoldt, et al (2018) was adapted. CPM imaging was done on a Nikon Eclipse ME600 microscope, which has fitted with cross-polarization filter and a CoolSNAP-Pro camera by Media Cybernetics. Temperature control was handled by a Linkman PE 94 and LTS-120E Peltier system. The preheated samples were filled into glass capillaries with a cross section of 0.3 x 0.03 mm, which were sealed on both ends using 3 M Scotch cyanoacrylate glue and fixed in place on microscope slides. To prevent sample contamination, an air bubble was kept on both ends of the capillary. During measurements, the temperature was first ramped to 60^0C, kept isothermally for 15 min, cooled to 30^0C at a rate of 10^0C/min, and then cooled to -2^0C at a rate of 0.2^0C/min. The temperature was held at -2^0C and imaging was done within the time frame of 30 – 60 min of the isothermal period.

Pour point measurement

The pour point of each waxy crude oil sample with and without the PPD was measured at a certain temperature range of 5-50^0C based on the standard of ASTM D5853 (Standard Test Methods for Pour Point of Crude Oils). The SARA and HEC analysis were performed according to the method reported by Coto *et al.,* (2022). Details are presented below:

SARA Type Separation: The purpose of this method focuses on determining the content of saturated, aromatics, resins, and asphatenes in crude oil. It is based on the ASTM D2549-02 standard test method which some modifications related to the removal of asphaltenes and the stationary phases used. In the first stage of SARA type analysis, asphaltenes and insoluble resins should be separated by precipitation with *n*-pentane (crude oil/solvent ratio equal to 1/30 vol.). The filtered sample (malthene fraction) is later split in a chromatographic column to obtain saturated compounds, aromatic, and polar resins [Coto, *et al,* 2011]. Chromatographic separation of malthenes is carried out in an installation that comprises three glass columns packed with silica gel (Macherey-Nagel 0.071 – 0.160 mm/100 – 200 mesh) and alumina (Merck 0.063 – 0.200 mm/70 – 230 mesh). A stream of nitrogen is also used to control liquid flow through the columns. In two of them, crude oil samples are eluted to check repeatability. The third column is used as a blank to detect potential problems related to the stationary phases. The different fractions are separated depending on their affinity to the solvent being used at each step of extraction. Saturated compounds are recovered passing through the column 85 mL of *n*-pentane [Coto, *et al*, 2011].

High-Temperature Gas Chromatography (HTGC): The experiments were carried out in a Varian Chrompack CP-3800 chromatograph, equipped with a Varian CP 7542 column 10 m long, 0.53 mm internal diameter, and 0.17 µm thick stationary phases. For detection, a flame ionization detector (FID) with a flame of air and hydrogen at a concentration of 430^0C was used. The method is based on the ASTM D-2887 analysis. The samples were diluted in carbon disulfide at a concentration of 5% by weight and injected on column. The carrier gas used helium, with a flow of 18 mL/min. The initial temperature of the column oven is 40^0C, and it is heated to 425^0C using a rate of 16^0C/min. The temperature remains constant for 20 min. For calibration of the retention times two different standard *n*-paraffin mixture were used: a mixture of $C_5 - C_{18}$ *n*-paraffins from Agilent Technologies and a $C_{20} - C_{70}$ mixture from Supelco called Poliwax 500 [Coto, *et al,* 2011].

Cold Finger Testing

The basic concept of the cold finger testing technique is that a cold surface (cold finger) is placed in a sample of heated crude oil, and cooling fluid is circulated through the interior of the cold finger. The cooling fluid is provided by a thermostated circulating heating and cooling baht. The oil is maintained at a temperature above the WAT. It is gently agitated about the cold finger with a magnetic stirrer. Deposits form on the cold finger's surface. The deposit gives a measure of the problem that can be encountered in the field that is producing the oil.

Test procedure for cold finger analysis:

Cold finger equipment was used to study the amount of wax at different conditions (Ridzuan, Adam, and Yaacob 2016b). The experiment was conducted for 3h and the water was maintained at 50^0C. The stirring rate of the impeller was varied from 100 to 600 rpm. The temperatures of the finger were set within the range of 5 to 20^0C. Ten milliliters of wax injected to the vessel for each run. Finally, the wax was scraped from the U-tube cold finger and weighed. The paraffin inhibition efficiency (PIE) was calculated using Eq. (1):

$$PIE\ (\%) = \frac{Wf - W\text{⍰}}{W\text{⍰}}\ \text{x}\ 100 \qquad (1)$$

Where w_f is the reference amount of wax deposition without chemical treatment (g) and w_t is the amount of paraffin deposition with chemical treatment (g) (Bello et al 2005).

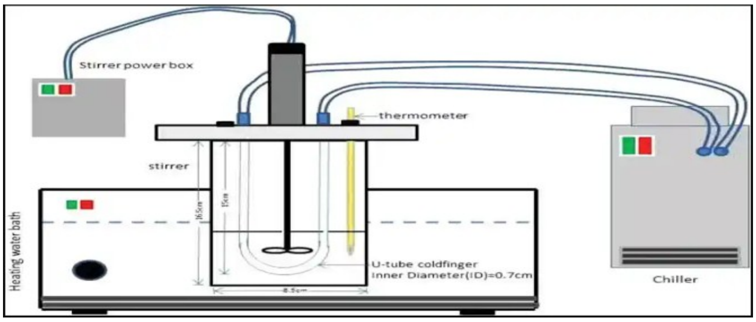


Fig. 9: Cold finger apparatus set-up (Ridzuan et al. 2016a)

Deposition studies were performed for original and crude oil samples containing wax inhibitor. A U-shaped cold finger was used to study the crude oil wax deposition. A measured amount of crude oil sample was in a cylinder. Cylinder was hanged in a thermostatic bath. Cold finger device, attached with low temperature thermostatic bath (chiller), was immersed in glass cylinder containing the crude oil. Temperature of chiller was kept 5^0C. Prior to study cold finger was weighed. Deposition was studied for 3 hours and readings were taken after every 30 minutes. I some designs, the oil is circulated inside the cold finger, which dips into a controlled bath of lower temperature. The amount and rate of deposit are measured. The temperature selected for the cold finger is the temperature of the field equipment where deposition occurs. If this is not known, the next lower known temperature is used. Various concentration of wax inhibitor are added to the crude oil.

Cold Finger Experiments

The effect of different parameters on the amount of wax deposition was investigated by cold finger setup and the effect of chemical inhibitors on WAT was studied. Different experimental tests were conducted in the cold finger setups. Several laboratory setups were used. The selection of wax inhibitors for crude oils has traditionally been performed using a “trial-and-error” approach. The performance of a series of chemical additives is evaluated using bench-top tests, such as pour point, cold finger, and rheology, and the best chemistry/dosage recommendations are made. The problem with the trial-and-error approach to the selection of wax inhibitors and pour point depressants is associated to the risk of selecting the wrong chemical.

One of the goals is to further investigate the validity of the hypotheses predominant in the literature regarding the effectiveness of wax inhibitors and responsiveness of crude oils. The experimental approach will be extended using Nigerian Crude Oil from the Niger-Delta region, on which effectiveness of polymer/clay nanocomposite additives was evaluated by using wax deposition test in a cold finger. Cold finger testing is used extensively for evaluating paraffin inhibitors for mitigating flow-line deposition. Cold finger testing has also been used for empirically predicting flow-line deposition, although these applications are less common. Cold fingers provide a simple, yet reliable, method to stimulate flow-line deposition, particularly for screening inhibitors. Equally important, only small sample sizes are required [Jennings *et al,* 2005]. Therefore, one of the objectives of this study was to gain a better understanding of the operation of cold finger apparatus. The entire test procedure was categorized into four elements:

1. Wax Appearance Temperature (WAT) Measurement
2. Cold Finger Testing
3. High Temperature Gas Chromatography (HTGC) analysis
4. Field Testing.

Figure 10: Cold finger device.

Wax precipitation and deposition in pipeline has been studied extensively over the years. Cold finger test conducted in the laboratory are widely used in the oil and gas industry for assessment of the paraffin deposition risk in export pipelines, subsea flow-lines and risers for identifying suitable paraffin inhibitors for deposition mitigation. However, a more effective treatment could be developed if a better understanding of the specific carbon chains contributing to the deposition (both in field and on cold finger) can be obtained. Such a distribution can be obtained by analyzing the crude oil and/or wax deposit using high-temperature gas chromatography (HTGC).

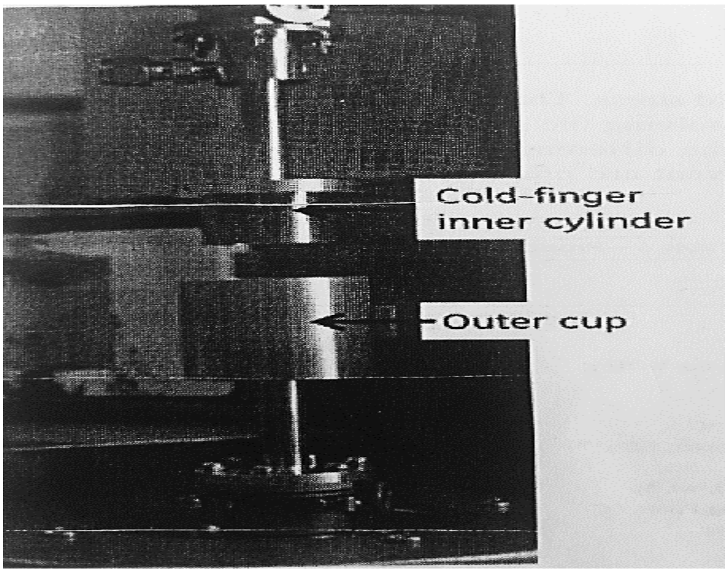


Figure 11: Cold-finger experimental set-up. Cold-finger inner cylinder is attached to the head of the rheometer and the cup outer cylinder is attached to the rheometer motor so that a constant shear is applied during the experiment.
Source: Adopted from: Peter L. Perez, et al (2016).

Wax Appearance Temperature (WAT) Measurement

Wax Appearance Temperature (WAT) of the crude oil was measured prior to carrying out the cold finger tests using Cross Polarized Microscopy (CPM). Laboratory experiments until recently were conducted using a Cold Finger Apparatus. A schematic diagram of the Cold Finger Apparatus is shown in **Fig 12**. The Cold Finger Apparatus is suitable only to measure the total mass of the deposit at the end of the experiment. The deposition rate cannot be measured. Furthermore, it uses only small volume of crude to conduct an experiment that could lead to misleading results. The observed deposition behavior using this apparatus is not entirely field-like and there is reason to question the field applicability of the results (Hunt, 1961). Because the Cold Finger Apparatus suffers from these drawbacks, a setup that would simulate the deposition in wells was formulated, according to the design reported by Brian F. Towler and Surya Rebbapragada (2004).

The procedure reported by Brian F. Towler and Surya R. (2004), was adopted. A laboratory-scale paraffin deposition flow system was constructed to simulate the deposition of paraffin in the wells. A schematic diagram of the system is shown in Fig 12.

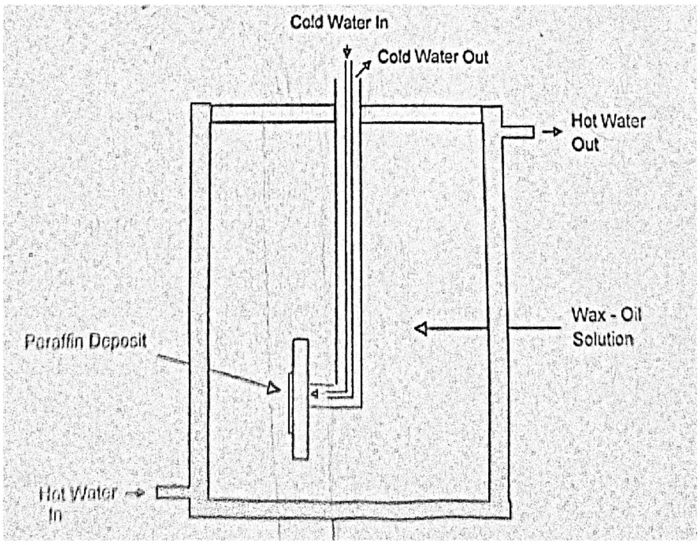


Fig. 12: Cold finger apparatus

Concentric tubes with a facility to measure the pressure drop between the ends of the inner tube which is called the test section. The crude that is used to conduct the experiments is stored in a reservoir, with a capacity of 10 gallons (0.0378 m^3). The crude can be pumped through the test section and back into the reservoir. The flow rate is adjusted using a flow meter and a bypass valve. An inclined manometer is used to measure the pressure drop. The manometer was inclined at an angle of 35^0 to the horizontal and the manometric fluid is water. Because water and oil have densities that are close to each other, this maximizes the mamometer reading. Thermocouples to monitor the temperature in the test section and in the reservoir were installed. A blower was required to keep the pump from overheating as the experiments were run for periods of 72 h.

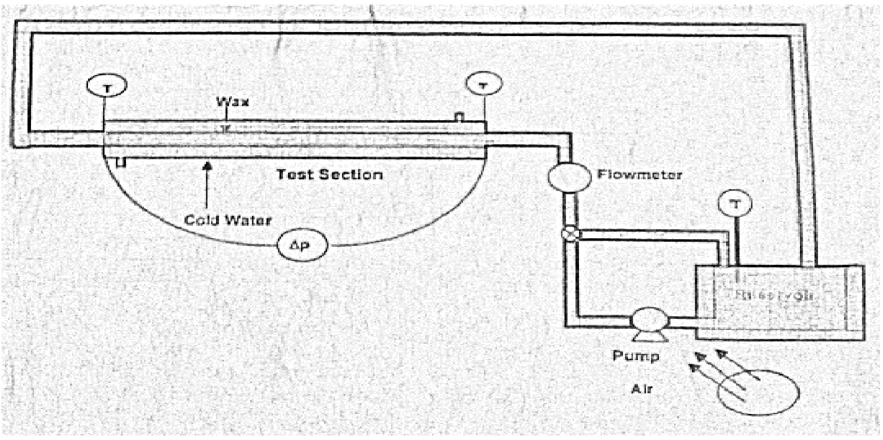


Fig. 13. Paraffin deposition flow system.

A water bath attached to a refrigeration unit was used to provide the cooling for the outer wall of the inner tube. The water was maintained at a constant temperature as required by the experiment. Water is pumped into the outer tube and back into the water bath. This keeps the walls of the test section at the required temperature throughout the experiment.

At the start of the each experiment, the manometer is checked to ensure zero reading, and the flow rate adjusted using the bypass valve. Manometer readings are noted at regular intervals until the end of the experiment.

At the end of each experiment, all the pumps and coolers are switched off, and the test section disassembled. Paraffin wax that is deposited in the test section is removed using scrappers and the amount of paraffin is measured using a measuring jar.

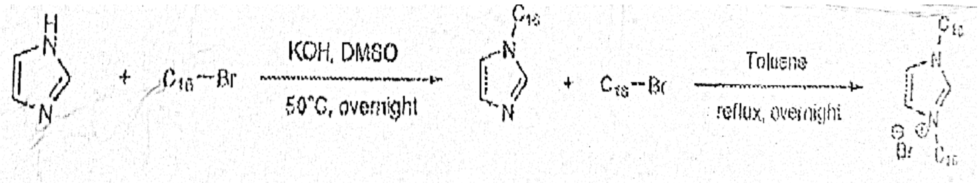
Field Application

For comparison purpose, the evaluation was done in a similar way reported by Bello *et al*, (2005). The chemical was injected from a designated point along the flow of Omoku-west T. Crude oil samples at both the upstream (near-well head) and downstream (manifold) locations of the injection point were carried out on daily basis for 11 days. The criteria used to evaluate the effectiveness of the injected chemical are the relative magnitude of the pour point, viscosity and API gravity of the produced crude before and after chemical treatment.

RESULTS AND DISCUSSION

Synthesis of imidazolium salts

The present study relates to an improved process for the synthesis of dialkyl chain imidazolium salts (imidazolium organic modifiers) with high thermal stability, high organic character and corresponding modified nanoclays with high d-spacing to prepare nanocomposites of various polymer composites, especially semicrystalline thermoplastics, such as PMMA.



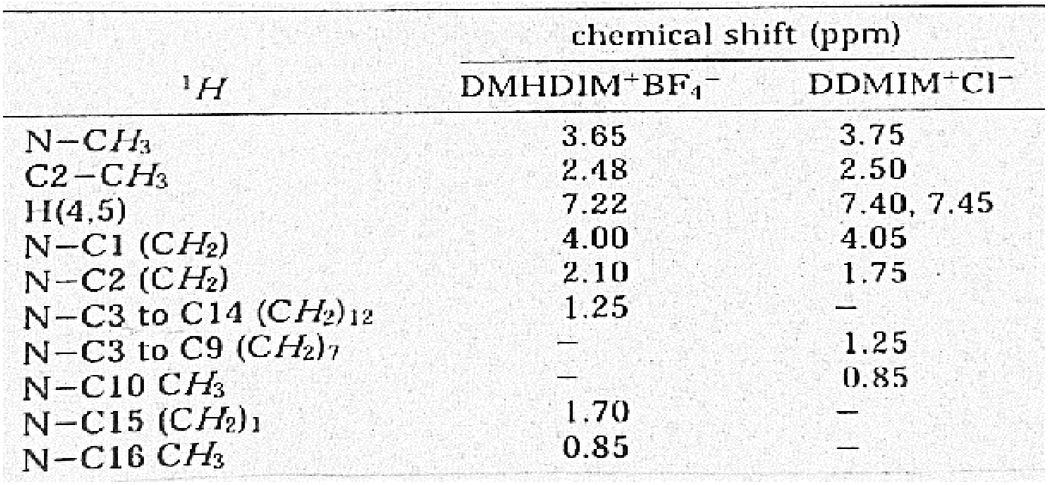
The synthesis procedure is described in more detail in Starikova, O.V.; Dolgushin, G.V.; Larina, L.I.; Komarova,; V.A. ARKIVOC (Gainesville, FL, United States) (2003), (13), 119-124

Several alkylimidazolium salt derivatives were prepared with propyl, butyl, decyl, and hexadecyl alkyl chains attached to the imidazolium through one of the nitrogens. The 1-alkyl-2,3-dimethylimidazolium bromide or chloride salts was a white precipitate. Typical yields were 60% - 80%. Non-halide counter salt was anions, such as BF_4, PF_6, were synthesized via ion exchange using an excess of the ammonium salt, such as NH_4PF_6.

The results indicated that the imidazolium cation is thermally more stable than the alkyl ammonium cation. This observation has been reported by others [Ngo *et al.*, 2000]. The type of the anion has an effect on the thermal stability of the imidazolium salts. The hexafluoro phosphate, tetrafluoro borate and bis(trifluoromethysulfonyl)imide salts show more than 100^0C increase in the onset decomposition temperature compared to the halide salts [Awad *et al*, 2002].

The products were characterized via mass spectroscopy (MS). ^{1}H and ^{13}C NMR spectroscopy, and thermal gravimetric analysis (TGA); the characterization data are consistent with data published on similar dialkylimidazolium structures.

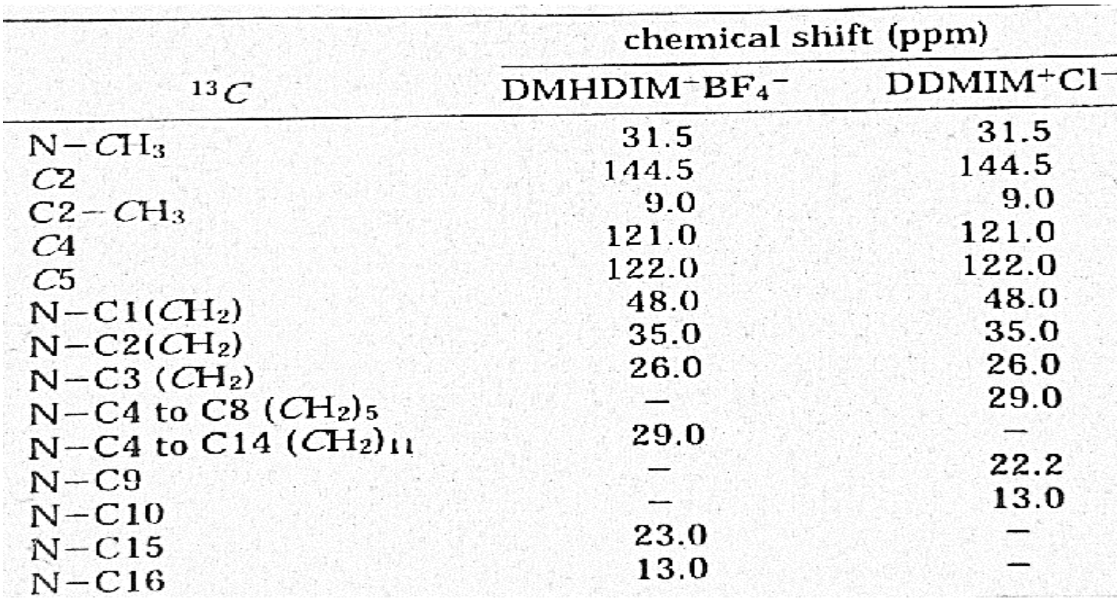
Table 5: ^{1}H NMR Data for 1-Decyl-2,3-dimethylimidazolium chloride ($DDMIM^+$ Cl^-) and 1,2-Dimethyl1-3-hexadecylimidazolium Tetrafluoroborate ($DMHDIM^+$ BF_4^-)^a



^1H	chemical shift (ppm) $DMHDIM^+BF_4^-$	chemical shift (ppm) $DDMIM^+Cl^-$
$N-CH_3$	3.65	3.75
$C2-CH_3$	2.48	2.50
H(4,5)	7.22	7.40, 7.45
N−C1 (CH_2)	4.00	4.05
N−C2 (CH_2)	2.10	1.75
N−C3 to C14 $(CH_2)_{12}$	1.25	–
N−C3 to C9 $(CH_2)_7$	–	1.25
N−C10 CH_3	–	0.85
N−C15 $(CH_2)_1$	1.70	–
N−C16 CH_3	0.85	–

Source: Adopted from: Jeffery W. Gilman, Walid H. Awad, *et al* (2002).

Table 6. ^{13}C NMR Data for 1,2-Dimethy;1-3-hexadecylimidazolium Tetrafluoroborate ($DMHDIM^+BF_4^-$) and 1-Decyl-2,3-dimethylimidazolium chloride ($DDMIM^+Cl^-$)



^{13}C	chemical shift (ppm)	
	$DMHDIM^+BF_4^-$	$DDMIM^+Cl^-$
N−CH_3	31.5	31.5
C2	144.5	144.5
C2−CH_3	9.0	9.0
C4	121.0	121.0
C5	122.0	122.0
N−C1(CH_2)	48.0	48.0
N−C2(CH_2)	35.0	35.0
N−C3 (CH_2)	26.0	26.0
N−C4 to C8 $(CH_2)_5$	—	29.0
N−C4 to C14 $(CH_2)_{11}$	29.0	—
N−C9	—	22.2
N−C10	—	13.0
N−C15	23.0	—
N−C16	13.0	—

Source: Adopted from: Jeffery W. Gilman, Walid H. Awad, *et al* (2002).

Organo-Modified Montmorillonite: Imidazolium-Treated Layered Silicate

About ten alkyl imidazolium treated montmorillonite organocays were synthesized via a standard ion exchange procedure [Vaia, *et al*, 1994]. The imidazolium-MMTs were then analyzed and used for synthesizing PLSN; a list of imidazolium-MMTs synthesized are provided below [Awad *et al,* 2002 and this work]:

a) N_2N-dihexadecyl – imidazolium montmprillpnite
b) 1,2-dimethyl-3-propylimidazolium montmorillonite
c) 1-buty1-2,3- propylimidazolium montmorillonite
d) 1-decyl-2,3- propylimidazolium montmorillonite
e) 1,2-dimethyl-3-hexadecylimidazolium montmorillonite
f) 1,2dimethyl-3-eicosylimidazolium montmorillonite
g) 1,2-dimethyl-3-methoxyethoxyethylimidazolium montmorillonite
h) 1,2-dimethyl-3-ethylbenzeneimidazolium montmorillonite
i) 1-ethyl-3-methylimidazolium montmorillonite
j) 1-hexadecyl-2-methylimidazolium montmorillonite
k) 1-hexadecyl-3-(10-hydroxydecyl)-2-methylimidazolium
l) 1-butyl-3-methylimidazolium montmorillonite.

It has been reported that the delocalized imidazolium cation has better thermal stability than the alkylammonium and pyridinium cations [Gilman *et al,* 2002]. This can be seen in the table below:

Table 7: Thermal stability Data for Imidazolium and Quanternary Alkylammonium-Treated MMT[a]

Sample	Organic fraction (±0.05)	Onset decomposition temp (TGA (^{0}C)^{b}	Peak decomposition temp (DTA) (^{0}C)^{b}	Change in *d* spacing vs NaMMT (nm)
1,2-dimethyl-3-hexadecylimidazolium/MMT	0.25	343	406	0.72
1-decyl-2-3-dimethylimidazolium/MMT	0.17	320	432	0.49
1-butyl-2-3-dimethylimidazolium/MMT	0.13	340	448	0.16
1,2-dimethyl-3-propylimidazolium/MMT	0.13	340	445	0.20
Dimethyldioctadecylammonium bromide	-	221	223	-
Dimethydioctadecylammonium bromide/MMT	0.36	280	308	1.49
Dimethyl-di(hydrogenated tallow)ammonium/MMT	0.35	200	310	2.00

[a] MMT = montmorillonite.

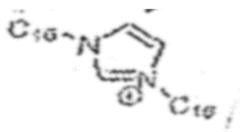
[b] Uncertainty for onset and peak T_{dec} measurement is ± 1.2 ^{0} C (2*o*).

Information relevant to utilize surfactants bearing one C_{16} alkyl chain for the preparation of poly(ethylene terephthalate) nanocomposites, as well as, poly(ethylene naphthalate) and other polymer matrixes (Davis *et al.* 2002, Maihotra *et al.* 2006, Zhoa *et al.* 2005, Morgan & Harris 2005, He *et al.* 2004, Bottino *et al*. 2003 and Kono *et al.* 2005).

The clays produced according to these references suffer from the disadvantage of a d-shaping below 25-26 Angstroms (A). In other words, the clays suffer from the disadvantage of a d-spacing below that of the widely used ammonium modified clays. Information relevant to attempts to utilizing imidalium salts bearing two C_{10} alky chains (Chua *et al.* 2006ab). Information relevant to use imidazolium bearing two C_{16} alkyl chains can be found in Wang, *et al.* (2003).

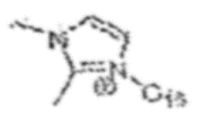
However, dialkyl imidazolium organic modifiers have higher d-spacing compared to corresponding monoalkyl modifiers. Information relevant to provide a d-spacing larger than 30A can be found in: Fox Douglas *et al*. (2007). The MMT can be modified by ion exchange with a modification of the procedure describe in Awad *et al.* (2004).

Clays can be prepared with imidazolium salts with one or two alkyl chains, for example:



D-2AI

N,N-dihexadecyl-imidazolium



D-AI

N-hexadecyl-imidazolium.

An N,N-dihexadecyl-imidazolium (D-2AI) modified clay was prepared and characterized as shown in the table below:

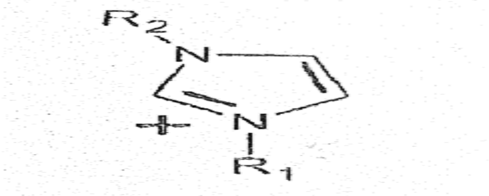
Preparation and Characterization of Alkly Imidazolium modified Montmorillonite

This work is based on the discovery that is now possible to make clays having relatively higher d-spacing with certain organic modifiers under certain conditions. It is advantageous to obtain such a relatively high d-spacing in clays, because the relatively higher d-spacing helps to obtain well-dispersed clays in nanocomposites, which in turn, helps obtain nanocomposites with better physical properties. The clays have excellent thermal stability and are particularly suitable for making PMMA based nanocompsites.

Table 8: Summary of d-s=acing and thermal stability of selected imidazolium modified clays.

Clay	d-spacing (A) from X-ray analysis	TGA analysis	
		T_{onset} (^{0}C)	T_{peak} (^{0}C)
N,N-dihexadecyl imidazolium modified clay (A)	31.31	353	428
1-butyl-3-methylimidazolium modified clay (B)	32.46	367	445
1-butyl-2-3dimethylimidazolium/MMT (C)	26.78	340	448

The results shown in the table above indicated that it was possible to make organic modified clay with imidazolium surfactant to obtain organic clays with d-spacing of clay with at least 28A and thermal stability of 350^{0}C from TGA analysis. This shows that it is possible to prepare organically modified clay wherein the clay is organically modified with an imidazolium sat of the formula



Wherein R_1 and R_2 which may be the same or different, are each a C_{12}-C_{25} alkyl group and wherein the clay is nanosized and has a d-spacing of clay intercalates of at least 30A and a thermal stability of at least 350^{0}C.

Selection of Organoclay for the Preparation of Nanocomposites

If the wrong organoclay is chosen for a particular polymer, the nanocompsite may never be formed as the nanoparticles might not disperse well enough. Further, even if the best organoclay is chosen, poor mixing or synthetic processes can result in a failure to form a nanocomposite, and in some cases, may result in a material with properties worse than the starting polymer. Finally, the target application will dictate clay loading, or whether clay is even acceptable for that final application. Tentative study showed that the imidazolium-modified clays in table 8 had better miscibility with PPMA. The miscibility of the imidazolium-modified in the PMMA matrix after melt mixing was examined by TEM. The TEM micrographs of neat PMMA and modified imidazolium clay in table 8 with PMMA materials are shown Figure 14. The first conclusion is that the evidenced morphologies were in the nanometer range, which can explain why the imidazolium clay and modified PMMA blends kept the initial PMMA optical properties.

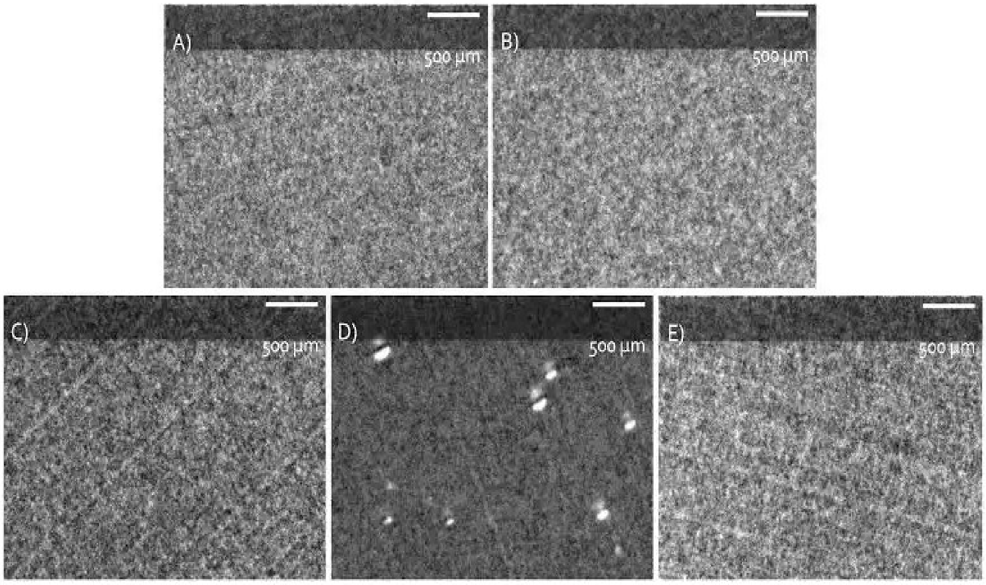


Figure 14: TEM micrographs of neat PMMA and imidazolium clay with modified PMMA materials.

(a) Neat PMMA;
(b) PMMA/1-butyl-3-methyl imidazolium modified clays
(c) PMMA/1-butyl-2,3-dimethyl imidazolium modified clay
(d) PMMA/N,N-dihexadecyl imidazolium modified clays

TEM micrograph did not show large difference between them. Such a phenomenon can be explained by the excellent miscibility of such imidazolium modified clays into the PMMA matrix. In general, the clays in their natural form are hydrophilic in natural are incompatible with most polymers. Surface modification and functionalization of clays helps in improving the compatibility with polymers and helps in dispersing the clay platelets in polymer matrix composites (Tcherbi-Narteh *et al.* 2013). The miscibility of 1-butyl-3-methyl imidazolium modified clay with PMMA, however, appears to be better than the rest. The 1-butyl-3-methyl imidazolium modified clay showed excellent compatibility with PMMA, hence was used for subsequent studies on the preparation of the polymer/clay nanocomposites.

Poly(methylcrylate)/organoclay nanocomposite prepared in supercritical carbon dioxide

Two crucial challenges of synthesis are to achieve; (1) chemical compatibility between the polymer matrix and the nanofiller at the nanoscale; and (2) homogeneous dispersion of the nanofiller within the polymer matrix. The interfacial interaction between nanoclay fillers and polymer matrix, as well as the quality of nanoclay dispersion, has a significant influence on the performance of polymer/nanoclay composites. These intercorrelated features determine the polymer/nanoclay composites morphology [Feng Guo *et al.* 2018]. The surface functionalization of nanoclay is a practical method to enhance the interfacial interactions between nanoclay fillers and polymeric matrix, enabling the transfer of interfacial stress from the polymer to the nanoclays [Feng Guo *et al.* 2018]. The result of this work showed that organo-MNT layers are well exfoliated and dispersed into the polymer matrix. Poly(methyl methacrylate) (PMMA) nanocomposites were successfully fabricated using melt blending as depicted below:

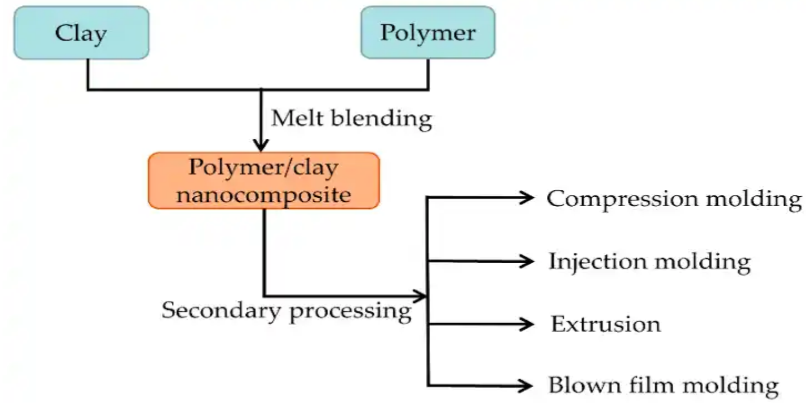


Figure 15: Melt-blending method scheme.

The properties of the nanocomposites increased with even small amount of clay addition. Therefore, to study the effect of clay content on the properties of PMMA nanocomposites, various PMMA/organoclay nanocomposites were prepared with 3, 5 and 7 wt% of nanoclay (relative to PMMA) melt blending method. Exfoliated nanocomposites were obtained at lower clay loading of <5wt% whereas an intercalated structure have been noticed at higher clay loadings. Similar existence of intercalated and partially exfoliated structure has been reported wherein PMMA/clay hybrids have been synthesized using emulsion and suspension polymerization technique. Several works have been reported on PMMA based nanocomposites synthesized by bulk polymerization of methlycrylate and by melt blending of poly(methyl methacrylate) [Lakshmi Unnikrishnan, *et al,* 2011]. In the present investigation the effect of nature of organically modified clays on the performance of PMMA nanocomposites prepared via melt blending have been evaluated. The exfoliation arrangement is of specific importance since it provides the highest interaction between the polymer and the modified clay by allowing the polymer to access the entire surface of the silicate layers, therefore resulting in the greatest variations in different physical properties.

The level of intercalation and exfoliation of the clay particles is highly influenced by the clay type, polymer, organic modifier, and the polymerization method. Three forms of polymer/clay composite configurations are possible based on the level of variation in the reaction between the layered silicate and polymer [Valapa *et al,* 2017] as discussed below and illustrated in the diagram in Figure 9, which contains transmission electron microcopy (TEM) images [Dalia E. Abulyazied and Antoaneta Ene, 2021] and wide-angle X-ray diffraction (WXRD) patterns of the structures of polymer/organoclay nanocomposites (phase-separated, intercalated, exfoliated).

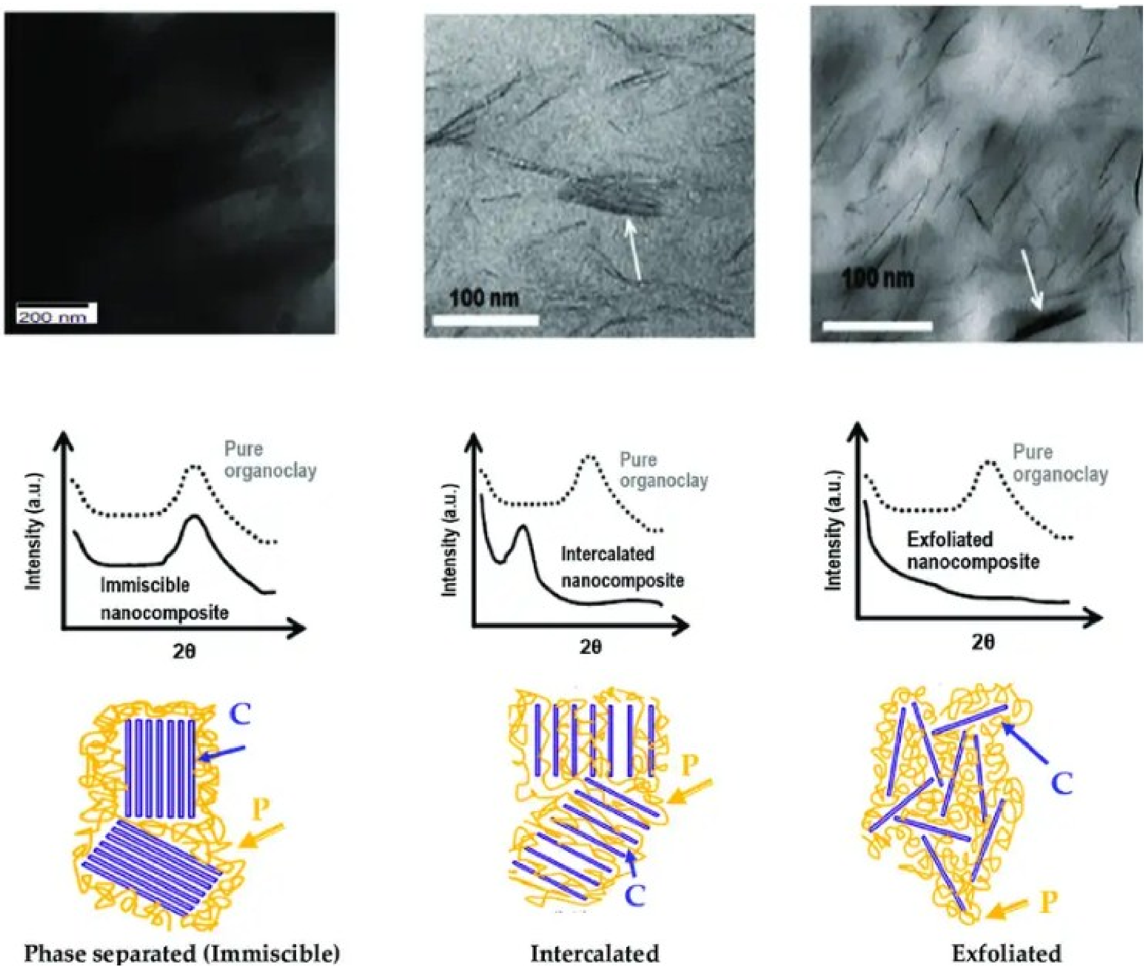
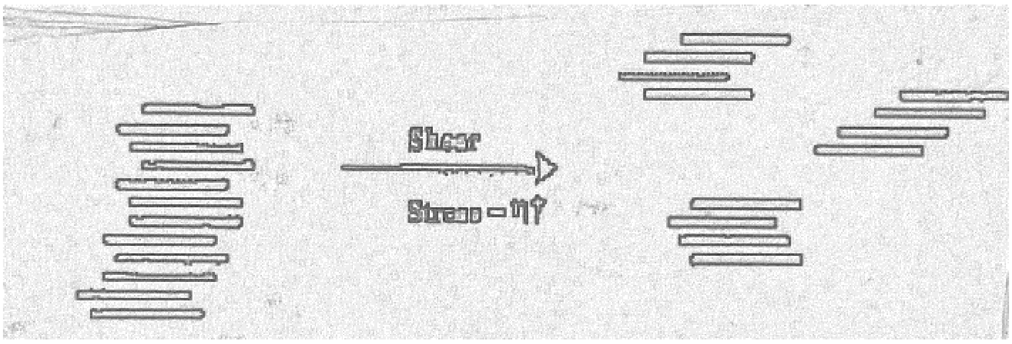
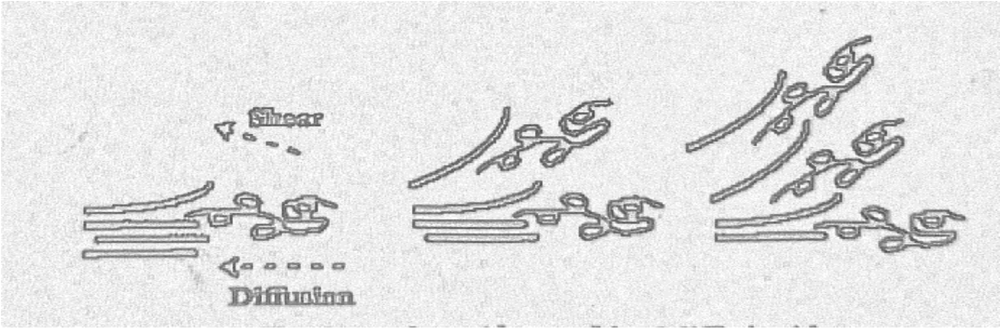


Figure 16: Illustration of various structures of organoclays (C) with polymers (p) (bottom) and their corresponding WXRD (middle) and TEM images (upper).

The intercalation/exfoliation of clay platelets was shown to be a combination of two mechanisms the breaking up of large stacks into smaller stacks of fewer and fewer clays platelets under the influence of large shear forces (Fig, 12a).



(a) Shearing of platelets stucks leads to smaller tactolds



(b) Platelet peel apart by combined diffusion/shear process

Fig. 17: Mechanism of intercalation/exfoliation of the clay platelets by the polymer (Fornes et al., 2002).

The clay galleries (Fig17b) also showed that higher the molecular the weight of the polymer matrix, the higher was its melt viscosity; greater was the stress exerted on the stack of clay platelets and the lesser was the number of platelets left in the stack.

Although the mechanism of intercalation/exfoliation by breaking of large clay crystals into smaller ones (Fig. 17a) and then peeling of the ends of the clay layers (Fig 17b) to allow the intercalation of polymer chains seems unlikely. Most likely the whole clay platelets at the top and at the bottom of a clay crystal would just separate out one after another by skewing under the influence of shear force since this would require less energy than that required for bending the ends of the clay layers and hence their ionic bonds with the neighboring platelets.

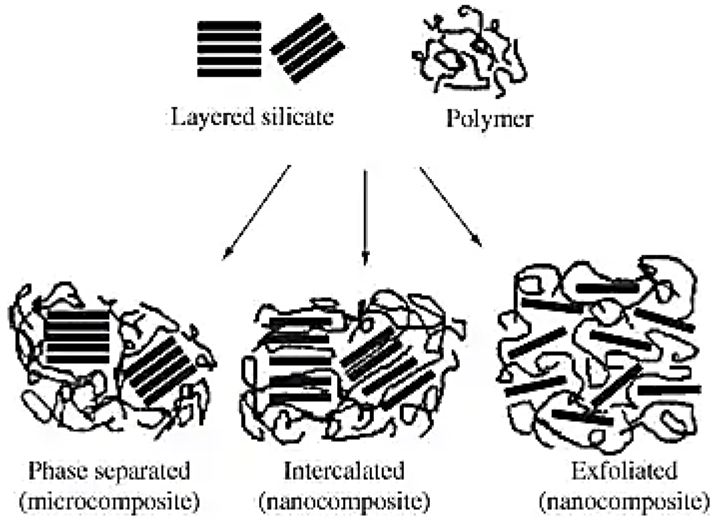
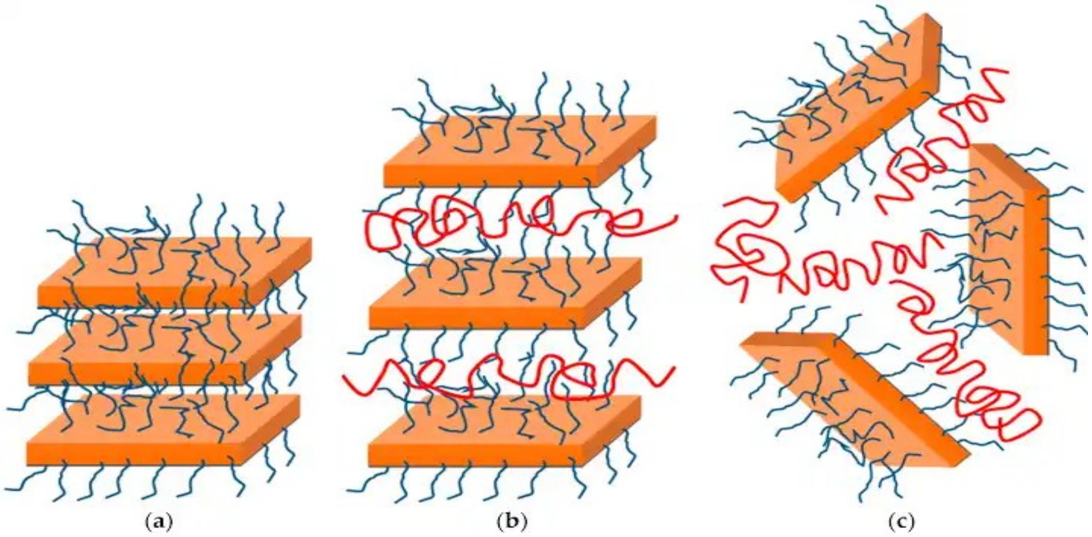


Fig. 18. Different structures of a polymer/clay nanocomposite (Alexandre and Dubois, 2000)

Structure and Morphology of the Nanocomposites

From both X-Ray Diffraction (XRD) analysis TEM it has been suggested that PMMA nanocomposites containing 1 wt % clay (C), 1 wt % (B) and 1% (A) are mainly exfoliated systems. Moreover, from the XRD patterns it was concluded that nanocomposites with 1 wt % clay (C) seem to be partially exfoliated, while for clay loadings higher than 1 wt % OMMT partially exfoliated and intercalated structures were revealed. The intercalated and exfoliated structures of the PMMA/OMMT nanocomposites together with a schematic illustration of neat OMMT appear in Scheme 1. Scheme 1a,b show indicative TEM photos of the PMMA/PMMT nanocomposites with 1 and 2 wt % clay (B) respectively, where organic phase is depicted as a bright area while clay nanoparticles occur as dark narrow bands. In each case, it is obvious that discrete clay layers may co-exist with two and three layer clusters into the polymer matrix. This implies that there is a part of organo modified MMT nanoparticles retaining its intercalate characteristic structure and thus yielding a partially exfoliated structure.



Scheme 1. Schematic illustration of neat organically modified montmorillonite (OMMT) (a) and of intercalated (b) and exfoliated (c) strucutres of the PMMA/OMMT nanocomposites (PMMA macromolecules are denoted in red colour).

Using clay as filler, two idealized nanocomposites are possible: intercalated and exfoliated. Intercalated results from the penetration of polymer chains into the interlayer region of the clay with preservation and crystallite delamination, with the individual nanometer-thick silicate platelets randomly dispersed in the polymer matrix. Exfoliated nanocomposites usually provide the best property enhancement due to the large aspect ratio and surface area of the clay. Technologically, useful polymer nanocomposites have not been investigated at higher filler loading (>10wt%). Thus far in most studies, only exfoliated nanocomposite structure with up to 5 wt% MMT can be achieved. To capitalize on the potential offered by nanoparticles in some area as higher levels of fully dispersed nanoparticles must be reached. The use of supercritical CO_2, if appropriately used, may lead to higher concentrations of exfoliated nanocly particles. Depending on the polymer, intercalated and exfoliated polymer/clay nanocomposites can be obtained by means of either mechanically compounding or in-situ polymerization. However, none of these means is easy and straight forward. Therefore, the use of SCFs to both pretreat/delaminate silicate layers and to reduce melt viscosity is an alternative means of generating well-exfoliated polymer/clay nanocomposites for certain systems. All the nanocomposites prepared were melt blended. The composition of each nanocomposite is calculated from the amount of clay and polymer charged to the extruder, as shown in Table. 9.

Table 9: Composition of poly(methyl methacrylate) clay nanocomposites.

Sample code	Inorganic clay in final product (%)	Modified clay amount (%)	Poly(methylacrylate) (%)
PMMA clay			
PMMA – 01	1	3.0	97.0
PMMA – 03	3	9.1	90.9
PMMA – 05	5	15.0	85.0

Polymer-clay nanocomposite could be developed by melt blending the polymer and an organophilic clay in a twin-screw extruder. In this route both polymer and clay are either simultaneously fed, or separately premixed and then fed, to the twin-screw extruder (Giannelis, 1996). The heat and shear generated by the screw in the barrel of the extruder facilitates the intercalation/exfoliation of clay in the polymer matrix. Various polymer-clay nanocomposites, using polymers like nylons (Fornes *et al.,* 2001), PET (Davis *et al.,* 2002), PET (Wang *et al.,* 2013), PP (Usaki *et al.* (1997) have been synthesized by this route. Being comparatively easier than the in situ route, the development of the melt blending route brought polymer-clay nancomposites to commercialization.

A thorough investigation of scCO-induced exfoliation of OMMTs has been conducted mainly by X-ray diffraction. Compared to the nanocomposites prepared without the aid of $ScCO_2$, the nanocomposites with $ScCO_2$ addition appear to have higher degree of nano-filler dispersion or intercalation/exfoliation [Yang Zhao, et al, 2006]. It was observed that for concentration as high as 6.6 wt% (limited only by present process capabilities), XRD peaks were eliminated, suggesting a high degree of exfoliation. Research has suggested alternative ideas about how the exfoliation process may occur in melt processing and how the details of the mixing equipment and condition alter the state of dispersion [Paul & Robeson (2008).

The structure of the organo nanoclay and the morphology of the nanocomposites were analyzed by wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM). A series of poly(methyl methacrylate) nanocomposites with imidazolium-modified MMT(bentonite) were prepared using a simple melt extrusion. The amount of clay content plays a vital role in controlling the structure of the nanocomposites.

Structural characterization of polymer/clay nanocomposite

In the preparation of a polymer/clay nanocomposite it is important to know the degree of intercalation/exfoliation and its effect on the nanocomposite moderate properties. In other word there is need to analyze the micro structure of the prepared nanocomposite. Two common techniques including X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM) are widely used to characterize the micro structure of nanocomposite as well as the bentoniteclay. Clays and organoclays show a characteristic peak in XRD analysis due to their regular layered structures. The peak is indicative of the platelet separation or d-spacing in clay structure. Using the peak width at half maximum height and peak position (2θ) in the XRD spectra the inter layer space can be calculated utilizing Bragg's law (eq.1).

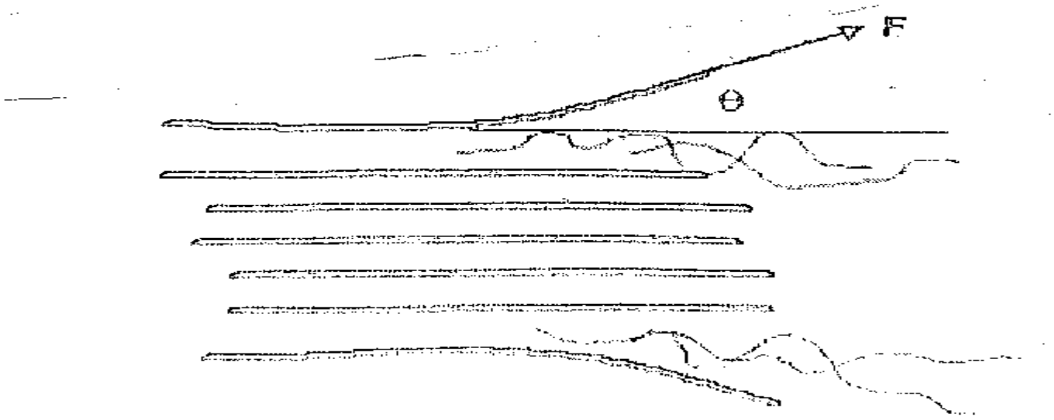
$$\text{Sin}\theta = n\,\lambda\,/\,2d$$

Where λ is wave length of X-ray radiation used in the diffraction experiments, d is the space between layers in the clay lattice and θ is measured diffraction angle. Any change in the inter layer or d-spacing of a clay lattice by organic modification or polymer intercalation causes to the change in the position, broadness and intensity of the characteristic peak in XRD spectra. According to the Bragg law, increasing of d-spacing results to the broadening and shifting of related XRD peak toward lower diffraction angles (2θ). By monitoring the position (2θ), shape and intensity of the characteristic peak for organoclay in nanocomposite structure it is possible to determine the degree of intercalation/exfoliation. The characteristic peak of MMT has been appeared at $2\theta = 7.13^0$ corresponding to the inter layer space of 1.24 nm. The XRD patterns of PMMA/organo MMT nanocomposites containing different clay percents (2-6 wt %) show diffraction peaks all shifted to lower 2θ degrees against the peak pure Na-MMT, which indicates the increasing of layers spacing due to the intercalation or exfoliation. The dispersion of clay in a polymer matrix is influenced by two factors: the choice of organic treatment for the clay and the processing or mixing method. Maximum benefits are achieved when the platelets as well dispersion or exfoliated. Exfoliated nanocomposites are formed when the individual clay layer break off the agglomerated particles or tactoids and are either randomly dispersed in the polymer (a disordered nanocomposite) or left in an ordered array. It is suggested that size reduction of clay particle and platelet delamination occur by surface peeling.

Mechanism of Clay Exfoliation in Thermodynamically Compatible Polymer/Clay System

The system investigated in details is poly(methyl methacrylate)/i-butyl-3-methyl imidazolium montmorillonite, which is a case of compatible polymer/clay system. In a thermodynamically compatible polymer/clay system, formation of nanocomposites can be greatly enhanced by appropriate choice of the mixing system and processing parameters. Dennis *et al* (2000, 2001), Cho and Paul (2001), and Fornes *et al* (2001) demonstrate the importance of processing conditions in the preparation of nanocomposites by melt compounding. They proposed two mechanisms for the exfoliation of clay platelets; (i) the height of the stacks of platelets is reduced by sliding platelets apart from each other; this process requires shear intensity and (ii) the polymer chains enter the clay galleries, thus pushing the ends of the platelets apart; this pathway does not require high shear intensity but involves diffusion of polymer into the chemical affinity of the polymer for the organoclay surface. The diffusion process is facilitated by residence time in the mixer [Nitin K. Borse, Musa R. Kamal, 2009].

For compatibility system of polymer/organoclay, where there is tendency to form hydrogen bonds between the organic modifier and the polymer matrix, polymer chains have strong affinity towards the organic modifier. In this case, the peeling of platelets at some angle may take place, as shown in Fig. 19. The shear stress required for peeling can also be calculated in terms of the peeling angle [Nitin K. Borse, Musa R. Kamal, 2009].



(a)

Fig. 19: Schematic representation of exfoliation process (peeling)

When polymer chains have affinity toward compatible clay surface, the polmer chains entering the organoclay galleries may initiate peeling at any angle above 0^0 [Nitin K. Borse, Musa R. Kamal, 2009]. It was shown that the compatibility between the clay and polymer, as well as the processing condition play important role in property enhancement of PMMA/clay nanocomposites. The processing system incorporating moderate shear stress but higher residence time was more effective in producing exfoliated nanocomposite structures and higher property enhancement. The proposed model shows that the exfoliation of clay particles is more likely to occur via a peeling mechanism. The breaking of the clay particles into smaller units (tactoids) by dispersion requires shear stresses which are higher than those available in extrusion processing. The peeling mechanism requires lower shear stresses which are achievable during melt extrusion. The exfoliation of the clay particles in polymer melts by peeling of platelets from the surface of the clay particles would require lower shear stress but longer residence time. In the case of compatible polymer/organoclay systems of PMMA/1-butyl-3-methyl imidazolium montmorillonite, polymer intercalation into the clay galleries initiates the peeling process at some angle, which results in a higher degree of exfoliation for the compatible system.

A thorough investigation of $scCO_2$-induced exfoliation of OMMTs has been conducted by x-ray diffraction. The starting material is a MMT intercalated with imidazolium cations. Many reports show that different processing technique based on supercritical carbon dioxide ($scCO_2$) constitute effective ways to increase dispersion and delamination in polymer/clay nanocomposites (Ma *et al.,* 2007; Nguyen and Baird, 2007; Treece and Oberhauser, 2007; Samaniuk *et al.,* 2009; Baker *et al.,* 2011; Feng-hua *et al*., 2011; Chen *et al*., 2012). X-ray characterization of most samples show the presence of basal 00/reflections, clearly indicating that treatments with $scCO_2$ induce organoclay exfoliation (Ma *et al*., 2007; Nuguven and Baird, 2007; Treece and Oberhauser, 2007; Samaniuk *et al,* 2009; Thompson *et al.,* 2009; Baker *et al.,* 2011; Feng-hua *et al*., 2011; Chen *et al*., 2012).

The changes seen in the XRD can be explained [Gilman J.W et al, 1999] by polymer entering the clay galleries pushing the platelets apart (i.e. intercalation). As more polymers enter the galleries, two possible changes can occur. First, the platelets can lose their ordered, crystalline structure and become disordered with the platelets no longer parallel without pushing the platelets apart. The result is that the XRD peak broadens into the baseline (intercalated disordered). Secondly, the polymer that enters the galleries pushes the platelets far enough apart that the platelet separation exceeds the sensitivity of XRD (exfoliation). TEM is a better tool to monitor dispersion because the clay platelets can be seen. The platelet count is a given area of the TEM photomicrographs, is used to describe dispersion; high values indicate a more delaminated and dispersed nanocomposite.

Physicochemical properties of the sample of Niger-Delta crude oil

Table 10: Characteristics properties of crude oil

Parameter	Observed Value
API Gravity	26.8
Pour Point	24^0C
Wax Content (%(w/w))	15.5
WAT	28^0C

Table 11: SARA analysis of crude oil sample

Components	Amount (%(w/w))
Saturates	66.82
Aromatics	10.11
Resins	17.80
Asphaltenes	5.34

The wax content, *n*-paraffin distribution, wax appearance temperature (WAT), and pour point, which defined the crude oil as naturally waxy oil, are measured via HTGC. From the data presented in Fig 20, it is clear that the concentration of 50 wt% of n-paraffin content in the waxy crude oil is situated between C24 and C47 and with high average carbon number of paraffin is 29.36. This range of n-paraffin has the ability to construct rapidly a massive interlocking network, which hinders the response of crude to additives at the proceeding stage of formation of fine wax crystal [Al-Sabagh *et al*, 2009].

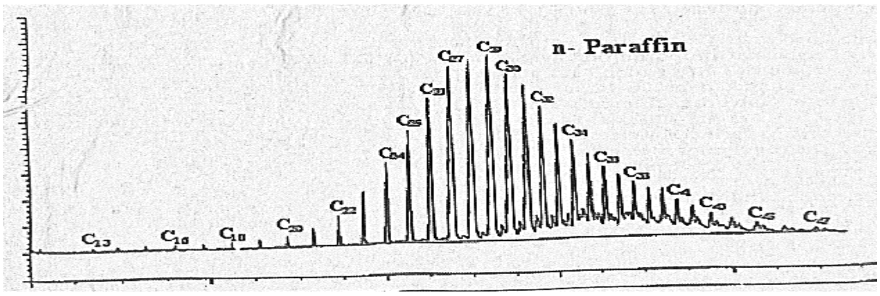


Fig 20: Carbon number distribution of n-paraffin in Niger Delta crude oil

Structural analysis of waxes carried out using ^{1}H and ^{13}C NMR spectroscopy indicated that these structures are mainly dominated by straight chains, with a low fraction of branching and also a low aromatic content. Surprisingly, this result is consistent with that reported by Al-Sabagh *et al* (2009). The saturate fraction of one crude oil was characterized using a SARA type analysis based on ASTM D2549-02. The *n*-paraffin distribution of the raw crude oil was determined by HTGC from its saturate fraction [Fig-20]. The wax analysis in the crude oil can be carried out with separation into fractions; the fractionation into saturated, aromatic, and polar (resin and asphaltene). The determination of the wax content was executed by quantifying the peaks of *n*-alkanes detected by high temperature gas chromatography (HTGC). Similar results were observed in 2006 by Jennings and Weispfennig.

High Temperature Gas Chromatohraphy (HTGC) for Wax Analysis

High Temperature Gas Chromatohraphy (HTGC) has the advantage of high column efficiency, high sensitivity, fast analysis speed and ease to be combined with other analytical methods (e.g. Mass Spectrometry). Thus, it is widely used to analyze crude oil and its products. Because of the limited thermal stabilities of capillary column and the stationary phase, the maximal column temperature of conventional GC is around 325^{0}C, and the analysis is limited to hydrocarbons with carbon number less than about 35. This fact limits the GC applications on the analysis of alkanes of high carbon numbers (C_{40+}) which are important for some areas including organic geochemistry.

During the past decades, high temperature (325^{0}C - 450^{0}C) GC (HTGC) has been developed rapidly and used for components of high molecular weight in crude oil, etc. compared with conventional GC, HTGC significantly extends the range of detectable hydrocarbons. Therefore, HTGC has become more and more routinely used for wax analysis, and the HTGC results can be correlated to the physical properties of the wax, including melting point, refractive index and kinematic viscosity (Gupta & Serverin, 1997). Figure 21 shows a typical HTGC chromatogram of a waxy crude oil. With a calibrated column, the relative area under the curve for each n-alkane will be converted to the relative abundance of the species. The reported n-alkane composition will be the amount of each n-alkane chain number and relative or absolute abundance (see an example as shown in Figure 22).

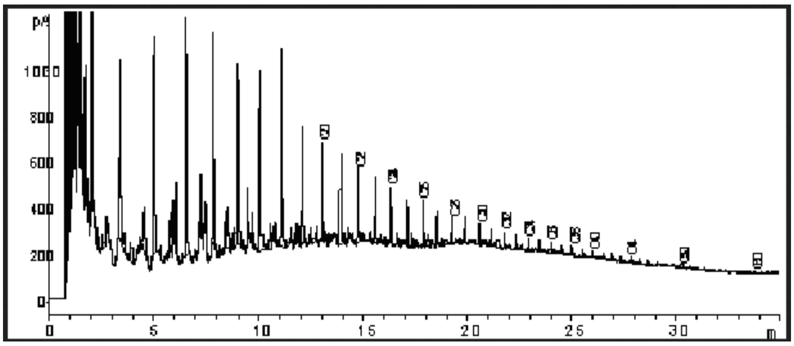


Fig. 21. Examples of HTGC traces of a crude oil

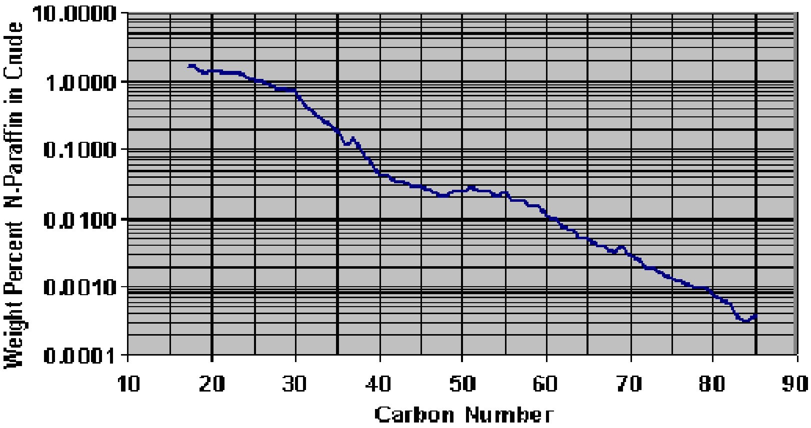


Fig. 22. n-paraffin distribution for a waxy crude oil analyzed by HTGC
Source: Adopted from: Huang Zeng, *et al* [www.intehopen.com]

Carbon Number Distribution

Gas Chromatography (GC) is the most utilized method used to quantify the composition of crude oils. The conventional GC is limited to the analysis of hydrocarbons with carbon number less than C_{40+} due its operational temperature of about 325^0 [Zeng *et al*, 2005]. High temperature gas chromatography (HTGC) with operational temperature range of about $(325\text{-}450)^0$C is much more suited to characterize high n-paraffin distributions usually associated with waxy crude oils. HTGC provides a simple and convenient method for determining n-paraffin distribution of crude oils. A complete characterization up to carbon number C_{100} can be completed in about one hour with HTGC [Zhu *et al*. 2008]. Alboudware et al (2006) stated that HTGC provides the most meaningful method of measuring the wax content because it determines the n-paraffin composition at each heavy end carbon number as high as C60 to C100. Similar study was carried out for the Niger-Delta Crude Oil and the result has been presented below:

Compositional Analysis

Compositional analyses of waxy crude oils are essential to accurately predict phase behavior and physical properties of waxy crude oils over a wide range of conditions. This will in turn help to provide solutions to wax related problems in crude oil production and transportation.

Saturates, Aromatics, Resins, Asphaltenes (SARA) Analysis

SARA analysis determines the susceptibility of crude oils to deposition of wax solids, and thus the stability of the crude oil. Deepstar IV Project (2001) is of the opinion that SARA analysis can provide a good source of information for waxy crude oil characterization and reports that SARA data has been used by some models together with the compositional analysis to predict wax phase behavior [Nwachukwu *et al,* 2015]. It is important to note that the extent of wax problem varies and can only be ascertained by laboratory analysis of crude oil samples specific to those fields/regions. The practice of validating thermodynamic and wax deposition models developed for a specific region with data generated from crude oils of different regions should be discouraged.

Analysis of Wax Deposits: The total content of the cold finger deposits consist of both wax species physically depositing and crude oil entrained within the deposit matrix. To determine the wax content of the cold finger deposits, high temperature gas chromatography (HTGC) analyses were performed on the deposits. In the HTGC analysis method used, qualification of *n*-alkanes peaks was accomplished using a valley to valley integration procedure [Jennings *et al,* 2006]. For the crude oil studies, the waxes were actually verified as predominantly *n*-alkanes – verified by NMR analyses on wax isolated. An example of a wax deposit HTGC analysis is shown in Figures 21-24. It is a cold finger deposit from the crude oil.

In addition to measuring the actual amount of the total deposit or amount of deposited wax to gauge inhibitor performance, indications of inhibitor performance often can be gained from visual assessment of cold finger deposits. Cold finger deposits from crude oil treated with an effective paraffin inhibitor often have portions of the cold finger surface which are bare from deposit due to "effective" deposit being sheared off by the flow field [Jennings *et al,* 2006]. Crude oil solids and waxes up to C_{60} can be analyzed by HTGC to determine *n*-alkane carbon number distributions. An additional benefit of the HTGC technology is the direct application to high – temperature gas chromatography-mass spectrometry (HTGC-MS; Fig. 3), which can be used in ion monitoring or in SCAN mode to provide critical data for the identification of individual peaks (Fig. 24) [Dahdah and Wavrek, 1997].

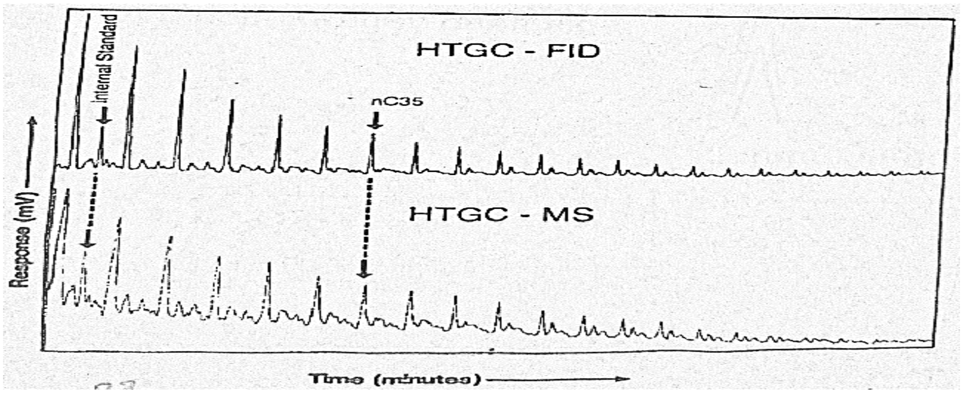


Figure 23. Illustration of the response from different HTGC detectors. The flame ionization detector (FID) is routinely used for monitoring the response of hydrocarbons eluting from the column, although the results can be directly compared to data obtained with a mass spectrometer (MS). The HTCG-MS data in this illustration are displayed as a total ion count (TIC). ***Source:*** Adapted from: N.F Dahdah and D.A. Wavrek, 1997.

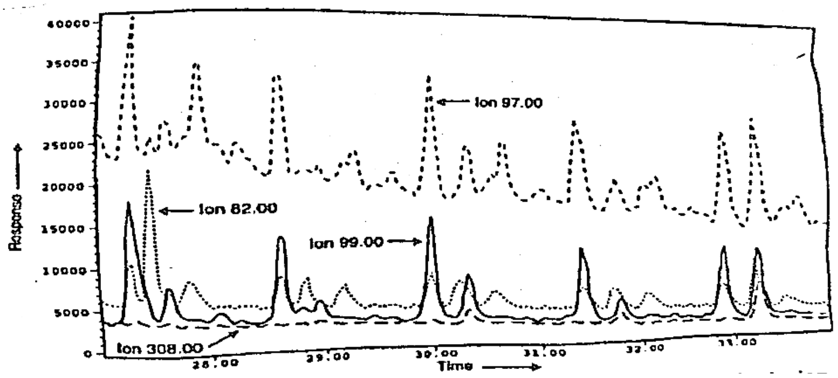


Figure 24. Illustration of the HTGC-MS data displayed as single ion monitoring (SIM) analysis to aid in the identification of individual peaks. The signal obtained from different mass-to-charge (m/z) ratios will show enhanced response from particular compounds: n-alkanes (m/z 99), n-alkylcyclohexanes (m/z 82), and methyl-n-alkylcyclohexanes (m/z). The m/z 308 trace is used to monitor for a parent mass (molecular weight of entire compound).
Source: Adapted from:N.F. Dahdah and D.A. Wavrek, 1997.

Deo and Wavrek (1997) used HTGC/MS methods previously described Wavrek and Dahdah to qualitatively demonstrate that the composition of crude oil solids obtained from deposition on cold surface as described by single carbon number (SCN) distribution is dependent upon bulk oil temperature and cold surface temperature. The Deo and Wavrek study (1997) also showed a difference in SCN distribution obtained by HTGC analysis of a solid deposit obtained from a pipeline versus a solid deposit created in a cold finger experiment from the same crude oil.

This paper has provided result of an investigation conducted to study the compound present in the high-molecular-weight fraction of Niger-Delta Crude Oil by high-temperature gas chromatography (HTGC). The focus of this research is investigation of the compositional variability of compounds in the HMW range. Specifically, it can be demonstrated that the composition of the paraffin fraction is dependent on the origin of the organic matter in the correlative source rock facies (Carlson and others, 1993; Wavrek and Dahdah, 1995).

Characterization of High Molecular Weight Paraffins in Niger-Delta Reservoirs

Problems related to crystallization and deposition of paraffin waxes during production and transportation of crude oil cause losses of billions of dollars yearly to petroleum industry [Ahmed Hammami *et al,* (1997)]. In recent years, paraffin (wax) deposition has created diverse production problems in many of the world's oil-producing regions. Often the problem is more severe for offshore fields where solutions to rectify wax precipitation can be costly [Ahmed Hammami *et al*, (1997)]. The failure of traditional methods to predict the precipitation of solids phases can be partially attributed to an inaccurate understanding of the molecular composition of HMW components. According to theory, the cloud point is needed to estimate the temperature at which paraffin will crystalize; usually, this value cannot be determined directly. Instead, the cloud point is indirectly estimated using techniques such as Differential Scanning Calorimetry (DSC). Interpretation of these data is difficult due to variation in the physic-chemical equilibrium and interactions between alternative molecular phenomena. Techniques that attempt to model the precipitation process assume HMW compound distributions that may be invalid (e.g., carbon number distribution, compound type). Fortunately, the HMW assemblage now can be determined directly using high temperature gas chromatography (HTGC) [Dahdah and Wavrek, 1997]. Significantly advances in the control of paraffin deposition can be anticipated when HTGC is used to quantitatively determine the distribution of the HMW components (C_{40+}) in crude oils. This research investigated the compositional variability of compounds in the HMW ranges using HTGC. HTGC analysis indicated the presence of compounds exceeding nC_{60} (Fig. 25). Features identified the HTGC that appear to be indigenous to this group of oils include enhanced nC_{41}, nC_{42}, and nC_{51} alkanes. High-temperature gas chromatography (HTGC) using capillary columns provide quick qualitative identification of *n*-alkanes present in waxes up to C_{90}.

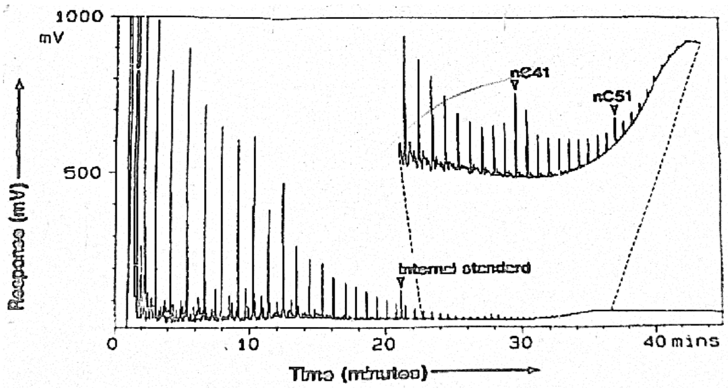


Figure 25: HTGC analysis of crude oil from Niger-Delta region of Nigeria. In the figure above the high-molecular-weight (HMW) alkanes extend beyond nC_{60} and that nC_{41}, nC_{42} and nC_{61} display an enhanced abundance. For the comparison, the result of conventional gas chromatography is presented in Figure 26 (below).

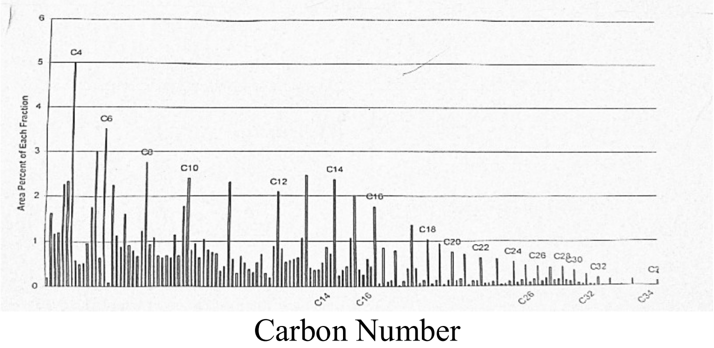


Fig. 26: GC analysis of Niger-Delta crude oil

Performance of Wax Inhibitor on the Deposition Behavior of Waxy Crude Oil

Wax inhibitor is the synthesized poly(methyl methacrylate)/Alkyl imidazolium modified bentonite nanocomposite, specifically PMMA/1-butyl-3-methyl imidazolium modified montmorillonite. It is also referred to as additive.

Paraffin Inhibition Efficiency of PMMA/1-butyl-3-methyl imidazolium Modified Clay Nanocomposite

WAT Determination (ASTM Standard D5773-04, 2005)

WAT is also called the cloud point [Merino-Garcia *et al,* 2008]. Lately, some researchers have shown the advantage of calculating wax disappearance temperature (WDT) compared to WAT. WDT is the temperature at which the last wax crystal melts. The WDT is thermodynamically more precise because crystallization requires some saturation [Hammami *et al,* 2003]. The efficiency of paraffin inhibition (total PIE) for total deposition can be calculated as [Ridzuan *et al*, 2016]:

$$\text{PIE}_{\text{total}}\ (\%) = \frac{Wn(\text{c11}-\text{c44}-Wi(\text{c11}-\text{c44}}{Wn(\text{c11}-\text{c44})} \text{ x } 100$$

Where $W_{n(C11\text{-}C44)}$ is the total amount of paraffin deposits without inhibitors (mg) and $W_{i(C11\text{-}C44)}$ is the amount of paraffin deposit with added inhibitor (mg) [Wang *et al*, 2009]. The effect of the wax inhibitor on ΔWAT and inhibitor efficiency in wax deposition is shown by Table 12 below.

Table 12: Effects of wax inhibitor/concentration (ppm) on ΔWAT, and inhibitor efficiency in paraffin deposition

Inhibitor	concentration (PPM)	ΔWAT (^{0}C)	$\text{PIE}_{\text{light}}$ (%)	$\text{PIE}_{\text{heavy}}$ (%)	$\text{PIE}_{\text{total}}$ (%)
250	Poly alkyl enamine	-2.7	71	13	52
500	Proprietary	-3.3	87	75	83
750	Polyolefin amide alkene amine	0.1	18	-9	9
1000	Polyolefin amide alkene amine	-0.2	33	3	23
1250	Poly acrylate	0.0	42	28	37
1500	Poly alkyl acrylate	3.4	72	18	54
2000	Olefin amide copolymer	-1.7	55	-3	36

As the concentration increase above 1500-ppm, no improved behavior was observed. Therefore, the actual optimal inhibitor dosage is a huge concern in the oil field due to cost and environmental aspects. However, 1500-ppm was considered as the optimal concentration, which corresponds to the maximum dosage of inhibitor required to provide maximum inhibition.

Table 13: Effect of nanocomposite (additive) on the pour point of crude oil

Additive concentration, PPM	Pour Point of Crude oil, ^{0}C
0	24
125	18
250	16
500	13
1000	7

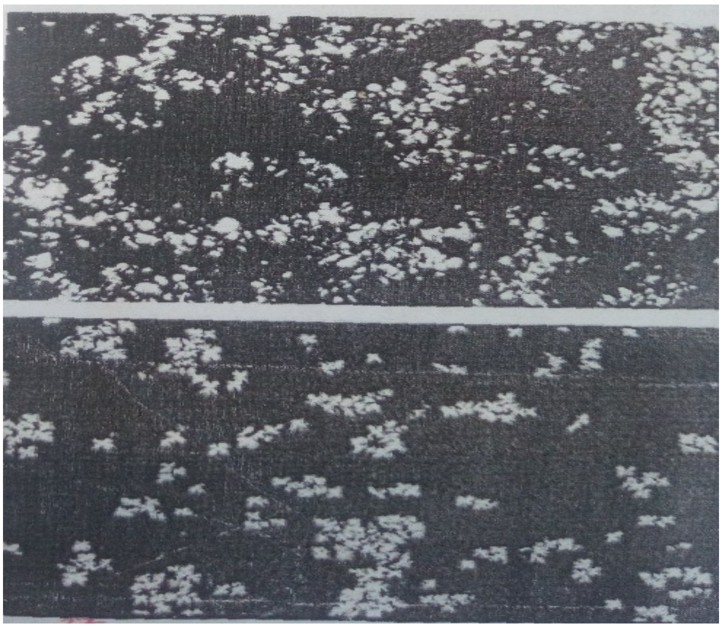
1500	2
2000	3
2500	23

Additive is PMMA/1-butyl-3-methyl imidazolium/modified clay nanocomposite.

The polymer/clay nanocomposites considered in this paper are crystal modifiers. These are substances capable of building into wax crystals and alter the growth and surface characteristics of the crystals. One effect utilized in oil production is the reduced tendency of the crystals to stick to metal surfaces such as pipe walls. Besides, the crystal modifiers will have the effect of reducing the tendency to form a three-dimensional network, thereby lowering the pour point as well as the viscosity. Hence, the name pour point depressants are also used for this class of chemicals. The result presented in table 13 requires understanding. As stated earlier, the polymer/clay nanocomposites studied here are wax crystals modifiers. Wax crystal modifiers are chemicals capable of growing into wax crystals and to alter their growth and surface properties. These chemicals reduce the affinity of crystals to interlock and form three-dimensional networks, thereby lowering the pour point and the viscosity. For that, they are commonly named pour point depressants (PPD). Pretreatment of crude oil with those chemicals is an attractive alternative to solve wax deposition problems during transportation of crude oil along pipelines [Coto *et al,* 2014].

Effect of Crystal Modifying Additive

The tendency to form crystal aggregates as seen in Figure 3b became even more pronounced and clear in the presence of the nanocomposite. A number of commercial additives of the poly(alkyl methacrylate) ethylene vinyl acetate (EVA) copolymer types have been found to depress the minimum pour point of oil far below 0 ^{0}C. Effective additive all had in common that they caused the formation of regular, spherulitic crystal aggregates, like those shown in Figure 3c, which were formed in the presence of 1500 ppm (w/w) of nanocomposite. Similar spherulite structures have been reported by Lovell and Seitzer to be formed in PPD-treated oils as well as neat shale oils. Hence, the flow-improving effect had to be chiefly due to the organization of needles and plates into weakly interacting sherulitic structures. It should be mention that the cross-like appearance of the structures in Figure 3c is an optical artifact. The cross remains stationary on rotation of the stage, indicating that they are actually spherically symmetric with single crystals arranged radially like in bog cotton [Hans Peter *et al*, 1991].



Since paraffin characteristic and contents vary drastically from reservoir to reservoir, production problems and their solutions vary accordingly. Methods that are effective in one system are not always successful in other reservoir or even in wells within the same reservoir. Effective paraffin inhibitor selection has the potential for substantial savings when compared against removal procedures. For this reason, it is fundamentally important to establish a good correlation between oil composition and paraffin inhibitors efficiency. To obtain more information about the influence of paraffin class fractions on petroleum wax crystallization and modifiers' behavior, concentration effects of the nanocomposite in the crude oil were investigated. A recent study demonstrated a clear correlation between oil composition and paraffin inhibitors activity (Garcia *et al.,* 1998a). Highly paraffinic crude oils were characterized showing very similar carbon number distributions (C5-C62) and well-defined maxima (C28).

For this reason, it is fundamentally important to establish a good correlation between oil composition and paraffin inhibitors efficiency. This leads to an adequate product selection for each particular case. It will also avoid extremely expensive and inefficient "trial-and-error" procedures (Garcia *et al.,* 1998a,b). The idea of a certain molecular weight range being affected by a given inhibitor is consistent with the fact that crystal modifiers normally consist of polymers with alkyl chain tails of a given length (typically 20-30 carbon atoms). The alkyl chain build into the crystals and therefore with their growth. Experiment data suggest that wax inhibitors somehow sterically hinder the wax molecules in a given molecular size range from precipitating until the temperature is several degrees below the thermodynamics precipitation temperature. This has little influence on the wax precipitation temperature because high molecular weight wax molecules (>C45) are apparently unaffected by the inhibitor, because the alkyl tail lengths of the polymers probably are too short to be able to efficiently build into the first wax crystals forming. There is probably some relation between the molecular weights of the alkyl substituents in the inhibitor molecules themselves. The wax molecules primarily consist of n-paraffins, i.e., straight hydrocarbon chains. A likely explanation of the inhibitor effect is inhibitor molecules with hydrocarbon chains of approximately the same length being built into the wax crystals. Side branches on the inhibitor molecules may prevent the wax crystal from growing until the temperature is further decreased and paraffins of lower molecular weight start to precipitate. If a relationship can be shown between the molecular weight or some characteristic chain length of the inhibitor and the molecular weight of the affected wax molecule, it will potentially be possible to design wax inhibitors suited for given oils and given operations [Pederson and Ronningsen, 2003].

However, specific levels of inhibition obtained in specific regions of carbon numbers by different paraffin inhibitor concentration have not been studied extensively earlier. This study presents a case study to demonstrate the need to look at performance of inhibitors on specific chains of carbon lengths to make a sound selection and also optimization of wax inhibitor concentration. Also, it has been observed in this current study that the untreated deposits obtained in laboratory cold finger test do not always represent actual field deposits. The carbon groups dominating the deposits in the field have been found to be different from carbon chain groups dominating the deposits obtained on the blank/uninhibited cold finger probs.

HTGC Analysis on Deposits

HTGC analysis was carried out on deposits obtained from the treated and untreated cold finger tests as well as on the paraffin samples obtained from the pig returns. The paraffin samples obtained from the field are the paraffins that actually deposited in the pipelines and can be analyzed through HTGC to get an idea of the kind of paraffins posing issues in the field. Figure 29 shows the carbon distribution of the field deposit (shown as percent paraffins on secondary Y-asxis) and cold finger test deposits (show as mass/area in g/m^2 on primary X-axis) of both blank and inhibitor treated samples for the test. It is fairly evident from the results presented in table 14 and Figs 28 and 29 study that looking at percentage protection figures from a cold finger test by different paraffin inhibitors concentration in blocks of carbon numbers can provide significantly different inhibition rates than the rate suggested by looking at the inhibition based on an overall difference in measure deposit weight on the cold finger test. The suggested approach gives a lot of useful information and insight into the performance of the inhibitor on specific groups of carbon numbers. This additional input on the performance of the inhibitors can significantly assist in better judgment and selection of the optimum concentration of the inhibitor for a particular application especially if information on the carbon number causing issues in the field is available. It is therefore possible to have a paraffin inhibitor which seems ineffective on a crude oil sample based on overall percentage protection may be effective in the specific range of carbon in which inhibition is desired. This trait shown by the inhibitor at the concentration of 1500 ppm where it showed an overall protection of just 27% but showed a significant inhibition of paraffin deposition in the carbon region which constitutes the majority of the paraffin deposit (83%). Usually, on particular paraffin inhibitor as concentration is chosen for an application. However, this study shows that different paraffin inhibitor's concentration might be the best performing ones in different regions of carbon range for the same application. C_{26}-C_{40} is the range of carbon numbers that is most dominant in field deposits. The result suggest that it might be a better practice to look into the percent inhibition of specific carbon groups that contribute to field deposits by analyzing the laboratory-obtained deposits through cold finger on inhibited and uninhibited cold finger probes using HTGC. Such an analysis gives a lot of useful insight and helps identify the performance or non-performance of paraffin inhibitors in regions of carbon groups where they are most desired.

Evaluation of Paraffin-Inhibition Efficiency (Low and high molecular weight paraffins)

The use of supercritical carbon dioxide led to higher concentrations of exfoliated organoclay. Thus, PMMA nanocomposites containing low organoclay loadings (3-5 wt.%) and high organoclay loading (10-15 wt.%) were investigated. In subsequent discussion, the nanocomposite containing 3-5 wt.% organoclay is designated inhibitor (A), while the nanocomposite containing oragnoclay is designated inhibitor (B). The WAT depression (ΔWAT) of the inhibitors on the crude oil is given in table 1. From the Table 1 the wax inhibitors tested did reduce the total amount of deposition and it seems that the inhibitors which are able to depress the WAT the most, are more likely to be effective in decreasing wax deposition. Because the WAT test detects the onset of precipitation and is biased towards seeing wax formation of the heavier alkanes **(Monger-McClure et al., 1997)**, inhibitors that depress the WAT the most may be those that have more effect on the higher molecular weight components.

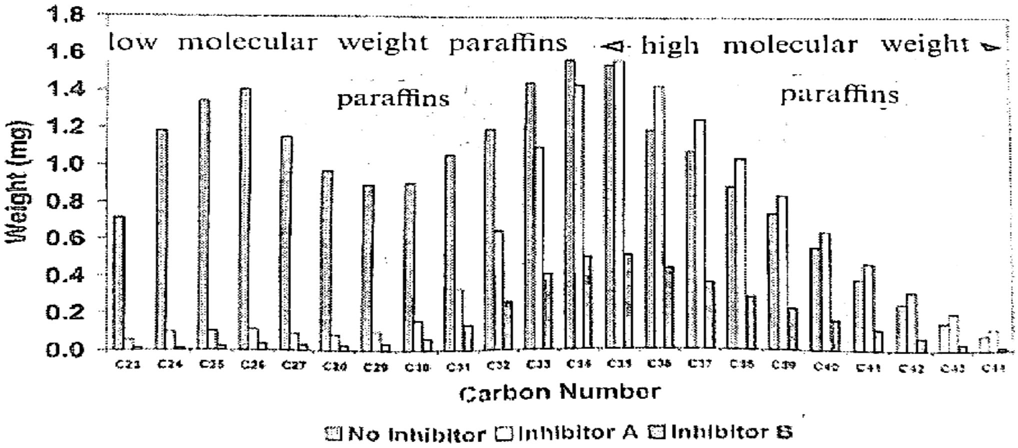


Figure 28: Effect of wax inhibitors (100 ppm) on paraffin deposition from a crude oil

Although Inhibitor B did reduce the deposition of the C_{34} and high molecular weight species, the relative inhibition of the low molecular weight is greater than the high molecular weight components.

High Temperature Gas Chromatography (HTGC) Analysis

High temperature gas chromatography (HTGC) can give the carbon distribution of a particular sample. It resolves the compositional characteristics of the complete n-paraffin distribution of a crude oil or of wax deposits. A Gas Chromatography column is used to separate the hydrocarbon components and the temperature is increased until all the components are eluted from the column. The eluted components are detected by a Flame Ionized Detector (FID) and the chromatograms generated are compared against those for standard solutions to evaluate the different components and their relative amounts.

The wax deposits obtained from the treated and untreated cold fingers are further analyzed for its carbon distribution using the High Temperature Gas Chromatography (HTGC). A certain fraction of the deposits are collected from the fingers and a GC sample is prepared using a solvent. This analysis was also run for deposit samples obtained from the field.

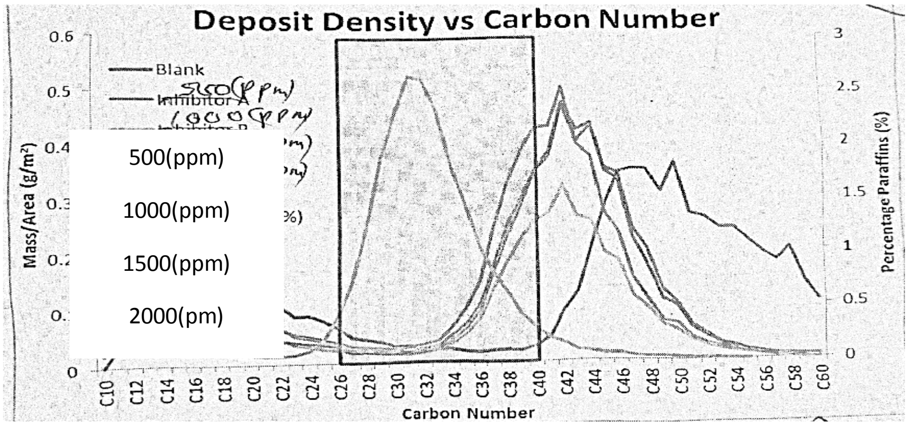


Fig. 29: HTGC Analysis of Field and Cold Finger Deposits

The field deposits are dominated by carbons from C_{26}-C_{40} region as seen from Figure 28. Therefore, the performance of the inhibitor tested in the cold finger test also analyzed in this specific region. The lower molecular weight carbons are dominant in the field deposits and that may be due to the configuration of production system. The oil sample gets cooled to a certain level of lower temperatures (lower than WAT) in this field before it is introduced in the pipeline which experiences paraffin deposits. The lower molecular chains may be the ones precipitating out in the pipeline facing depositions and hence, these carbon chains dominate the paraffin deposits in the field. Also, it can be seen that the blank deposits obtained from the cold finger tests do not have the same carbon distribution as the field deposits. The cold finger blank deposits have a higher weightage of higher carbon numbers in them compared to the field deposits. But the performance of the inhibitor in the highlighted region can still be carried out in the region of interest in the field. The percentage inhibition results in this region as compared to the percentage inhibition results based on overall paraffins are as follows:

Table 14: Comparison of Overall Inhibition C_{26}-C_{40} Region Inhibition

Concentration of inhibitor (ppm)	% Overall Inhibition	% C_{26}-C_{40} Inhibition
Blank	n/a	n/a
500	20	6
1000	-	-
1500	27	83
2000	21	9

Table 14 shows that while the inhibitor concentration of 1500ppm showed an overall percent inhibition of 27% but its percentage inhibition in the C_{26}-C_{40} region is 83%. The inhibitor starts giving higher mass/area at higher carbon ranges peaking at around C_{44}. This lower protection at higher carbon regions skews the overall percentage protection of the inhibitor.

Table 15: Effect of PMMA/1-butyl-3-methyl-imidazolium/modified MMT (composite) on properties of crude oil (Field test)

Day	Dosage/mg/kg	Pour point /^{0}C		Pour point reduction/^{0}C	Viscosity (30^{0}C)/mPa.s		Viscosity reduction /%
		Before treatment	After treatment		Before treatment	After treatment	
1	40	24	5	19	935	300	68
2	50	33	13	20	1172	60	95
3	50	33	15	18	763	19	98
4	50	37	23	14	1720	119	93
5	50	17	4	13	396	334	16
6	50	23	3	20	408	314	23
7	100	18	-5	23	1716	41	89
8	100	33	15	18	2365	256	89
9	11	1	-11	12	293	32	89
10	10	27	10	17	2418	476	80
11	50	33	22	11	192	48	75

CONCLUSION

The deposition or crystallization of wax paraffin from crude oil is one of the crucial issues faced in the petroleum industry particularly when the temperature of the crude oil is below the wax appearance temperature (WAT). The use of solvents (xylene and xylene mixtures) has been widely reported for treatment of paraffin (wax) problem in the Nigerian oil and gas industry but this technique does not prevent wax deposition. Therefore, relatively cheap wax inhibitions are developed as a preventive strategy to avoid an absolute wax deposition. The ultimate goal of this wax inhibitor screening program is to identify the candidate additives that are expected to perform the best in the field. The performance is optimized in terms of the type and concentration of additives used to formulate the package and treatment dosage. Pour point measurements, and wax deposition experiments in cold finger devices at different conditions aid in the final selection, complemented with empirical know-how about the influence of crude oil properties, field condition, etc., on the expected field performance. In the present work, the performance of the nanocompsite was evaluated on waxy crude oils from some locations, seeking to understand the correlation – either empirical or quantitative – between the observed wax inhibitor (nanocomposite) effectiveness and crude oil properties. Both chemical and physical properties of these crude oils were considered, from conventional physical properties such as API and viscosity, to SARA composition (saturates, aromatics, resins, asphatenes) and chemical parameter look into the percentage inhibition of specific carbon groups that contribute to field deposits by analyzing the laboratory-obtained deposits through cold finger tests on inhibited and uninhibited cold finger probes using HTGC. Such an analysis gives a lot of useful insight and helps identify the performance or non-performance of paraffin inhibitors in region of carbon groups where they are most desired.

Conclusively, judging from the pour point and other properties the naonocomposite observed for the field test, has evidently demonstrated a good performance and great potential for inhibiting wax deposition and achieving improved flow characteristics of crude oil at fairly low chemical dosage of about 1500 PPM. The study of the paraffin inhibitors concentration-based dependent could help in identifying different effective concentration in different regions of carbon numbers for the same application. This approach may also be used to test different inhibitor's concentration for their performance in different carbon regions and the results may be used to formulate a single chemistry which might be effective over the desired range of carbon chain distribution of paraffins.

This report summarized the synthesis and utilization of poly(methylmethacrylate) nanocomposite based on modified montrillonite. Increasing the thermal stability of organically modified layered silicates is one of the key points in the successful application of polymer layered-silicate nanocomposites on the industrial scale. To circumvent the detrimental effect of the lower thermal stability of alkyl ammonium treated montrillonite, a series of alkyl imidazolium molten salts were prepared and used for the preparation that requires melt-processing temperatures. The results also show that the imidazolium treated montrollonite has excellent compatibility with poly (methylmethacrylate) (PMMA) thus enabling preparation of polymer layered silicate nanocomposites. High temperature gas chromatography (HTGC) was used to determine wax content and n-paraffin (macro and micro-crystalline). The physical properties of the crude oil and molecular characteristics derived from high-temperature gas chromatography (HTGC) were used to seek correlation to wax inhibition performance. Dealing with flow assurance issues to the wax precipitation process require not only the assessment of the amount of precipitated wax but also a characterization of the precipitated solids. According to the HTGC-MS analysis of wax precipitated from oil at different temperatures, it was observed that wax formed at high temperatures (about 40^0C) consisted primarily of high molecular weight isoparaffins and condensed napthenes, while the n-paraffins become dominant at somewhat lower temperature.

The PMMA/MMT exfoliated nanocomposites exhibited the potential of wax inhibitor, alternatively known as pour point depressant (PPD)/wax crystal modifier. One effect utilized in waxy oil production is the reduced tendency of the crystals to stick to metallic surface. Besides, the wax inhibitors will have the effect of reducing the tendency to form a three-dimensional network, thereby lowering the pour point as well as the viscosity. Hence, the name “pour point depressant” is also used for this class of chemicals. Though the effectiveness of the use of solvents (xylene and xylene mixtures) has been reported in treating paraffin problems in Nigeria oilfields, the application solvents, like the mechanical removal of paraffin, does not prevent the further deposition of paraffin and sometimes the present accumulation of paraffin needs to be removed. Therefore, a program of additives undertaken to retard or prevent future building of paraffin is necessary. This is the ultimate goal of this work.

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Conflict of interest

There is no conflict of interest.

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