POLYMER MATERIALS AND NANOTECHNOLOGY FOR OIL AND GAS

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BIOGRAPHICAL NOTE

Dr. Rigoberto C. Advincula is Professor at Case Western Reserve University, Department of Macromolecular Science and Engineering. He is a Fellow of the American Chemical Society (ACS) and has recently received the Mark Scholar award of the Polymer Chemistry Division, ACS. He has published over 400 papers and is highly cited with an H-index = 41. He is Editor of the Journals *Reactive and Functional Polymers* and *Polymer Reviews*. He has been plenary and invited speaker to a number of international conferences and has held visiting professor positions at MPI-P, NUS, TUAT, and AIT. He has mentored 26 Ph.D. students and continues to mentor undergraduate and high school students as well. He obtained his Ph.D. at the University of Florida and did Post-doctoral work at the Max Planck Institute for Polymer Research and Stanford University. He consults and collaborates with a number of companies.

ABSTRACT

This paper summarizes the opportunity to investigate potential applications of new polymers and nanomaterials in the oil and gas energy industry. For the last 10 years there has been an increase in interest and research for new materials useful for upstream, midstream, and downstream processes to effectively find function in demanding environments including directional drilling and hydraulic fracturing. High temperature high pressure (HT/HP) and brine conditions pose a challenge for emulsification, demulsification, and viscosity of drilling fluids. This talk will give a short overview of the polymer materials requirements in the oil and gas industry, the opportunities and function for new structure and compositions, and the use of nanotechnology - graphene, graphene polymer coatings - nancomposites in high performance materials, drilling, well-logging, anti-corrosion, anti-scaling, and other additive materials.

PAPER

Polymers in Oil and Gas

Polymers are large molecules or macromolecules that derive their property based on size, composition, and ability to interact with neighboring chains or solvents (non-covalent interactions and cross-linking). Plastics is a most familiar term.[1] Although these days many everyday things from clothing to car parts to packaging are synonymous with material comfort. As a barrier or coating material, its properties are important in preventing chemical and physical degradation of the bulk phase that needs protection. On the other hand, as a packaging material, it is important to protect the outside environment from the contents of the bulk phase. A high number of these materials are classified as engineering materials and has to be fabricated through a number of methods from their corresponding resins. A number of abbreviations are as follows: polystyrene (PS), polymethylmethacrylate (PMMA), polyetheretherketone (PEEK), polyvinylchloride (PVC), polycarbonate (PC), etc. (Figure 1)[2,3]

Polymers (thermoplastics, thermosets, and elastomers) play an important role in many phases and stages of the oil and gas energy production. They can be divided into upstream, midstream, and downstream applications. In the upstream applications they include: drilling mud viscosity modifiers, dispersants, anti-corrosion, and anti-scaling agents, polymeric cement, elastomeric seals, thermoset coatings, thermoset parts - replacement of corrosion prone parts. The requirements are more demanding when going to high temperature/high pressure (HT/HP) conditions where degradation and creep is faster. This requires high performance polymers.[4] For offshore technology and sub-sea condition demands, there is also the requirement for marine environment durability. That means preventing plasticization and redox degradation mechanisms due to high salt conditions. Often, protective coatings have to approach almost hermitic sealing conditions to enable long-term durability to prevent creation of salt-bridges. This is also observed with requirements in the upstream applications for geothermal energy harvesting where HT/HP demands can be combined with high brine conditions and silication scaling. In drilling applications, they find uses that enable stability or viscosity control at various stages of drilling and completion. Polymeric cement is another interesting applications since setting (curing time) and viscosity control is important at various stages of casing development especially with directional drilling. In midstream applications, the use of pipes, coatings, and other mechanical applications in housing, parts replacement, is present. However, polymers play an important role in demulsification and as additives in controlling the transport of complex gas/liquid compositions of produced oil/gas. Often, water emulsion is a problem and lack of viscosity control can have enormous consequences in production rate and cost. Otherwise, the same demands for external environment applications apply. In the downstream role, polymers even play a more important role as additives with applications such as: anti-corrosion, anti-scaling, dispersants, emulsifiers, flocculants, viscosity modifiers, asphaltene control, etc. As additives they have solubility ranges from hydrophilic, lipophilic, and amphiphilic or surfactant properties. Hence solubility parameters and hydrophobic-lipophilic balance (HLB) behavior is important. The use of polysaccharides, polyelectrolytes and hydrogels are numerous. It should be noted that small molecule additives play an important role as well in many applications from upstream to downstream especially as additives fulfilling the same role as polymers but with a different phase and chemical behaviour.

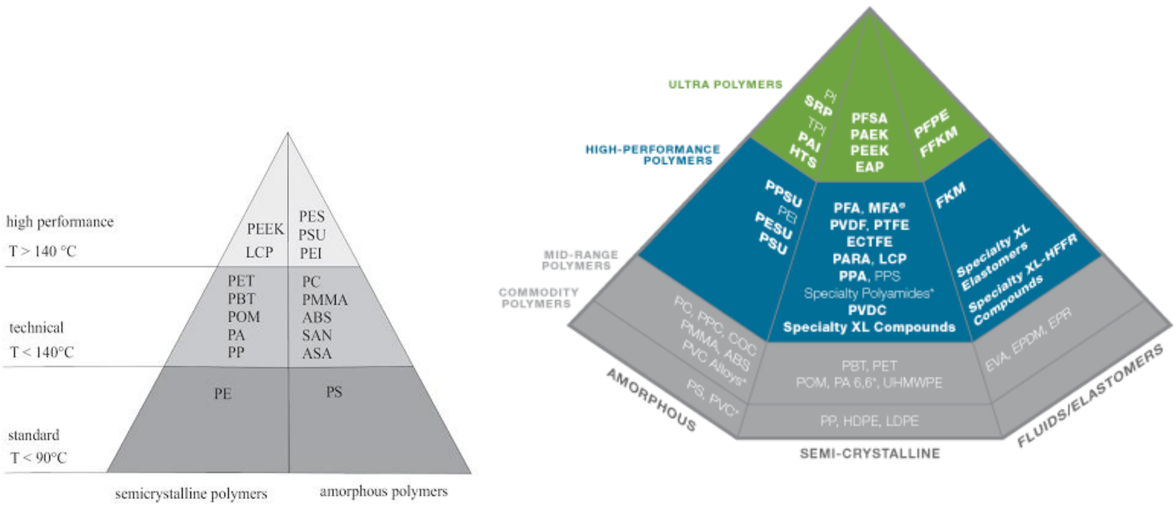

Figure 1. Hierarchy of polymer materials and their stability (Tg and Tm) and possible degradation correlation. (images obtained from Ref. 2 and 3)

One important role worth mentioning in detail is corrosion mitigation. A large amount or resources is often devoted to mitigating corrosion. Thermodynamically, corrosion is a very energetically favorable process converting a high-energy metal or metal alloy into its low-energy oxide form. Corrosion not only poses serious problems economically and industrially, but also endangers human life, i.e. structural failure and biofilm formation. It is very difficult to stop corrosion from happening completely. The only option is to slow down its rate by preventing aggressive oxidizing species from reaching the metal surface, or by having a sacrificial material that preferentially reacts in place of the metal. Once corrosion is observed, it is important to investigate the different pathways and sources of failure to prevent further degradation. Thus it is important to utilize effective mitigation strategies with new materials and coatings. Essentially, the use of nanomaterials can be in the form of inhibitors, inhibitor reservoirs, cross-linking agents, and nanofillers for improved coating durability.

Thus the role of polymeric materials as durable high performance materials and protective coatings is obvious and from these, one can add the use of nanomaterials as additives or as blended agents in enhancing the role of polymers in oil and gas energy.

Nanotechnology in Oil and Gas

Nanotechnology involves the applications of nanomaterials, nanostructuring (nanoengineering), and nanoscale phenomenon towards practical solutions. In the oil and gas energy services, there are a number of opportunities primarily related to interfacial phenomena and colloidal science. Another possibility is in the spectroscopic or catalytic signature of these materials. Here are several applications and research areas for oil and gas:

1) **Drilling:** Application in drilling and completions will involve materials and methods to drill and complete wells with increasing strength, durability and provide completion design options not possible with existing technologies. Nanotechnology for example has been used for formulating novel guar fracturing fluids. For example, the use of stabilizing nanoparticle dispersions in very demanding high salinity, high temperature downhole environments – since nanoparticles can act as very stable surfactants and rheology modifiers. Current drilling and completion methods are often faced by challenges and demands of increasingly hostile environments of new oil and gas finds both onshore and offshore. Applications of advanced drilling and completion methods will require materials performance beyond current technologies. Nanotechnology may provide unique solutions to these challenges. Applications of nanotechnology to cement, drill bit, and drilling fluid design is possible through new nanoparticles, alloys, and nanogels respectively.
2) **Reservoir engineering and production** – From upstream to midstream, the viscosity of oil is very important. Achieving low viscosity is essential for higher production in heavy oil wells. Increasing the temperature of heavy oil is a usual practice in lowering its viscosity and consequently, increasing productivity – but at a cost. Investigating methods of modifying the reservoir characteristics in particular with hydration control, helps release more oil from the formation. Can nanoparticles be used to induced more localized heating or delivery of higher heat capacity particles further in the formation? There is also interest in controlling the demulsification process to control oil/water mixture. Another interest is in the use of reservoirs for sequestering CO_2. Is it possible to use nanomaterials and nanoscale phenomena to increase the efficiency of CO_2 injection and enable predictions on the kinetics of mixing?
3) **Flow management issues** – This can be based on controlling scaling, corrosion, and paraffin formation. Can nanotechnology be used to mitigate these problems and therefore assure flow conditions well into the production phase? It is desired to have increased recovery, efficient reservoir sweep water management and use of chemically modified nanoparticles to achieve reservoir illumination for monitoring. For scaling control, this could involve the use of nanoparticle stabilized emulsions that are also sources of scaling and corrosion inhibitors. Stable amphiphilic Janus particles or anisotropic clay or graphene particles can be particular intriguing. The use of nanoparticle materials in enhanced oil well cement hydration and improved mechanical properties is also important.
4) **Inhibitors and Monitoring agents** – nanoparticles due to their nanoscale sizes are able to penetrate deeper and farther into the formation and therefore, mitigate problems at early stages or provide a better resolution of the reservoir formation. Nanoparticle inhibitors can be utilized to prevent corrosion, scaling - they can be effective nanoparticle sealants. Fluorescent nanoparticles can be used for real time reservoir monitoring. Depending on the nature of the particles, they can also aggregate at the surface and prevent fluid loss. Examples include applications in enhanced oil recovery (EOR) where the optimization of the well requires both preservation of the formation (for high yield) and mapping of the interconnectedness of wells and formation with sensors. They can also be particularly useful in HT/HP environments.
5) **Scaling control** in downhole conditions is important as delays or stops in production can be very expensive. The effect is not only on the downhole structure but also on the equipment. A main motivation is of course maintenance cost reduction. Can nanotechnology be used for unconventional scale control? Several examples of applications can include, the use of nanoemulsion anti-scaling agents - scale inhibitors based on reservoir and formation character and proper use of scale indexing and nanomaterial coating on the formation to prevent adhesion.
6) **Devices and Tools.** Nanoscale phenomena can also be used to produce better alloys, coatings, and composites. For example, it can be used for high strength in-situ self-corrodible metal composites and alloys for completions tools. A main driver is retention of function even at HT/HP and high brine conditions. New materials and sensors at this highly corrosive and demanding environments are needed. Knowledge gain on nanoscale phenomena in crystallization, annealing, dispersion of materials can be used for fabrication. Nanofabrication has been shown to create high resolution chemical sensors and robust sensors.
7) **Sensor and tracers** - Nanoparticles and other nanomaterials can be used to enhance various aspects of oil and gas exploration and production. Metals, metal oxides, chalcogenides, carbon based nanomaterials – their unique spectroscopic and catalytic properties, for example, can be viewed as the next generation of efficient tracers or agents. This can be done by introducing these materials as substitutes and alternatives for radioisotope tracers. They can also modify surfaces, interfaces and fluid properties, such as wettability and rheology. Because of their size and shape, the deep penetration of nanoparticles in oilfield formations can be a determining factor in designing successful nanotechnology-based treatments in the oil and gas industry.

Graphene Materials in Oil and Gas

Carbon polymorphs and nanomaterials include carbon nanotubes (single walled or multiwalled), fullerenes, and graphenes. Graphene is the simplest of all graphitic forms - it can be stacked to form 3D graphite, rolled to form 1D carbon nanotubes and wrapped to form 0D fullerenes. It is essentially a single-atom thick, honeycomb network of two-dimensional sheets of sp^2-hybridized carbon. Discovered in 2004, graphene with its long-range p-conjugation, has attracted tremendous attention for its exceptional structural, chemical, mechanical, thermal and electrical properties. These remarkable attributes have stimulated escalating interest for applications as field-effect transistors (FET), photovoltaics, biosensors and electrodes. Due to its outstanding transparency (97.7%), graphene is envisioned as the future of transparent, touch-screen and foldable electronic displays.[5]

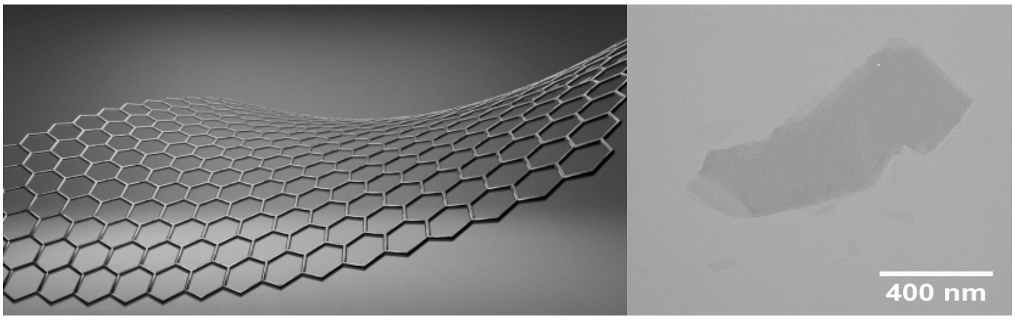

Figure 1. Graphene structure of 2-D fused aromatic systems and actual TEM image of isolated nanomaterial.

Some of the possible uses of introducing graphene into any material system includes: increased thermal conductance, reduced friction, reduced wear & tear, stable viscosity, higher load bearing capability and sensing or well-logging. These improvements would drive the applications of polymer nanocomposites and nanomaterials in the oil & gas industry to even higher performance. Here are a few examples of the applications of graphene:

1) **Sensing.** Graphene can possibly be used for well logging. Well logging protocols provide data and evaluation on the geological properties and map of reservoirs of interest. This is employed in the production phase (upstream). A commonly used logging technique provides information downhole by the use of wirelines. Wirelines are long wires with sensors attached at the end. These are lowered into an exploration hole to provide information about the hole, its contents, depth profile, and connectivity (or conductivity). An extension of wireline logging protocol is logging-while-drilling (LWD), which relies on sensors at the end of the drill itself. However, both methods utilize oil-based fluids for drilling and lubrication. The difficulty is that oil-based fluids are not very good conductors of electricity. This is ideal for the use of conducting graphene materials. The Tour group developed magnetic graphene nanoribbons (MGNRs). The MGNRs can form part of a conductive coating in oil-based drilling fluids, improving the reliability of the information relayed back up the hole by the sensors.[6] Furthermore, the magnetic properties of the ribbons could also be exploited as sensors. Because of the small size and the aspect ratio, MGNRs can be made small enough to pass into smaller fractures and crevices of the rock which can still hold extractable oil. As sensors, they can perhaps send wireless data which contains information on oil location and concentration. Tiny sensors coated with graphene could expedite the discovery of oil and natural gas reserves, As sensors in fluids injected down exploration wells, they can then move more efficiently through cracks and crevices in search of hydrocarbons. The interaction with graphene in particularly can be recorded as history or transmitted wirelessly to a receiver. Most oil wells are drilled vertically - drillers know what's happening at well A and well B, but do not know what is happening in the spaces between them. Such a technology will enable geomapping and explore deposits laterally. It can have interesting using with directional drilling and hydraulic fracturing.

2) **Drilling Mud.** The Tour group at Rice University first showed that adding graphene oxide (GO) platelets to the drilling operation has several advantages. Adding GO to a water-based drilling fluid blend decreased the losses of the fluid to the surrounding rock, as compared to a standard mixture of bentonite clays and polymers commonly used in the drilling industry. When the drill bit is removed and drilling fluid displaced, the formation oil forces remnants of the filter cake out of the pores - as the well begins its production phase. However, some clays remain, reducing the portent productivity. Pliable and “starfish like” flakes of GO can form a thinner, lighter filter cake - the flakes fold in upon themselves and look something like starfish sucked

into a hole. When the well pressure is relieved, because of the shape, the flakes can still be pushed back out by the oil with the latent pressure. The thinner graphene layers can then be extracted more easily than the layers from traditional clay-enhanced liquids. Thus with extraction, the GOs are rendered many times smaller than the flakes' original diameter by folding.

3) **Hydraulic Fracturing.** In hydraulic fracturing, proppants or propping agents are used to keep or "prop up" fractures in the formation after a drilling hydraulic fracturing phase. Often, this involves several stages. Although the bulk of this composition is water (99.5%), drillers need to add other chemicals and additives to the high volume of water. It will be of high interest to use produced water (water already in the ground) or seawater into the wells. However, high salt content (existing ions) and other hydrocarbons and aromatics can result in complex viscosity and fluid conditions that are hard to control once the drilling and completion phases are put into stage. As proppants, they can be used to fill gaps or go into very narrow fractures. Graphene and graphene oxide can be used as sensors and additives to relay data up to the surfaces – and army of sensors that can relay the data based on time (stages), distance, and depth profiling. As sensors they could detect gases or changes in the water/ oil chemistry as well as the interface of emulsions. As proppants and additives in the traditional sense, they can be used as surfactants and amphiphilic agents capable of controlling the pH, viscosity, and emulsification process. By derivatizing GO with complementary hydrophilic groups, ligands, and ionic groups, they can augment the performance of existing additives and have the sensor reporting function. Like any additives, they have to be evaluated by their cost-effective ratio.

4) **Coatings.** Graphene oxide based nanocomposites and other polymer-filler materials can have superior coating performance based on controlled wetting and conductivity. The preparation of graphene-polymer electrodeposited films have been shown to have controlled wetting properties, conductivity, patternability, and even anti-microbial properties has been demonstrated by our group. The latter is important for preventing biofilm formation and preventing MIC corrosion. Patternabiliy and template deposition has been demonstrated with graphene oxide – polyvinylcarbazole composites.[8,9,10]

CONCLUSION

Numerous opportunities are possible with the use of new polymer systems and nanomaterials like graphene in the oil and gas production. This has been enumerated for upstream, midstream, and downstream applications. The classification of polymer materials into thermosets, elastomers, and thermoplastics can easily categorize their use as coating and engineering materials. However as additives, their solubility and viscosity is of high importance. Nanomaterials include metals, inorganic oxides, semiconductors, organics, and carbon based materials will find increasing use in the oil and gas industry as their salient properties are reported in specific applications. Graphene in particular has some interesting applications based on its size, shape- aspect ratio, and conductivity. In the future, such convergence of the use of polymers and nanomaterials in the industry will be a matter of cost-effective ratio studies, where even a small amount of the latter can make a difference in high performance and efficiency of operation.

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