Waste to Want: Polymer nanocomposites using nanoclays extracted from Oil based drilling mud waste

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Waste to Want: Polymer nanocomposites using nanoclays extracted from Oil based drilling mud waste

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Abstract. Due to the European Union (EU) waste frame work directive (WFD), legislations have been endorsed in EU member states such as United Kingdom for the Recycling of wastes with a vision to prevent and reduce landfilling of waste. Spent oil based drilling mud (drilling fluid) is a waste from the Oil and Gas industry with great potentials for recycling after appropriate clean-up and treatment processes. This research is the novel application of nanoclays extracted from spent oil based drilling mud (drilling fluid) clean-up as nanofiller in the manufacture of nanocomposite materials. Research and initial experiments have been undertaken which investigate the suitability of Polyamide 6 (PA6) as potential polymer of interest. SEM and EDAX were used to ascertain morphological and elemental characteristics of the nanofiller. ICPOES has been used to ascertain the metal concentration of the untreated nanofiller to be treated (by oil and heavy metal extraction) before the production of nanocomposite materials. The challenges faced and future works are also discussed.

1. Introduction

Oil based drilling mud also called oil based drilling fluid and non aqueous drilling fluid, is a mixture of base oil (petroleum), bentonite clay or lime, barite and other chemical additives used for oil and gas exploration [1]. Drilling fluids are used to remove and bring to the surface, cuttings generated by the drilling bit as the well is drilled. However, drilling fluids (see figure 1) have become a potential source of pollution thereby increasing the environmental footprint.

The main concern about oil based drilling fluids emanate from the base oil used to produce them and the reservoir hydrocarbons they may interact with during drilling (also for water based fluids). The oils (Diesel or mineral oil) contain polycyclic aromatic hydrocarbons (PAH) [2]. The PAHs are cytotoxins. PAH is a colourless, sweet smelling and highly flammable hydrocarbon. Under European Union directive of dangerous substances (Directive 79/831/EEC); amended from Directive 67/548/EEC, EU regulation 1907/2006 - REACH (Registration, evaluation, authorisation and restriction of chemicals) information on substances notified under Directive 67/548/EEC and DSEAR – Dangerous substance and explosives atmosphere regulation 2006, petroleum oil is described as a carcinogenic, mutagenic and toxic due to PAH presence [3].

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During Exploration and production (E&P) activities, the drilling fluid and cuttings generated are brought back to the surface (the top-side of the platform). At this location the drill cuttings are separated from the drilling fluid using the solids control equipment before it is tested for rheology and reused for further drilling activities. However, when the rheology of the drilling fluid is lost, the use of the drilling fluid is discontinued. Figure 2 illustrates the fate of the used drilling fluid during and/or after the drilling process.

Figure 1. Spent (used) Drilling Mud [2]

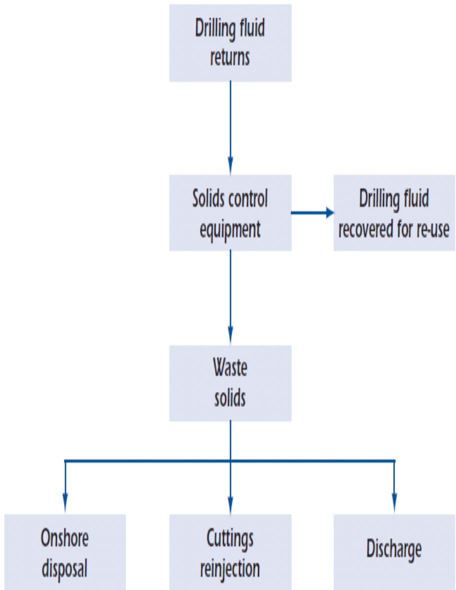

Figure 2. Fate of the Used Drilling Fluid [2]

Different methods have been proffered as solutions in the management of hazardous wastes generated from oil and gas E&P activities. However, some solutions are highly energy and power consuming, generating loads of greenhouse gases and other forms of environmental hazards. Some of these methods include: landfilling, road spreading, phytoremediation, bioremediation, subsurface drilling waste re-injection, ocean dumping, mechanical, chemical, thermal, stabilisation and solidification. Drilling fluid wastes have been used to make different products such cement base products, levees, tar road bases [6]. In our pervious research, we had developed an eco-sustainable (environmentally friendly), biodegradable non-toxic chemical treatment for the extraction of oil and water from the spent drilling mud through phase separation to obtain oil pure water and solid for reuse and recycling.

1.1 Environmental legislation supporting Recycling

According to the European Parliament, under Article 4 of the EU Waste Framework Directive (WFD) (2008/98/EC) the waste management hierarchy for waste prevention and management involve the following: prevention, preparing for re-use, recycling, recovery, e.g. energy recovery, and disposal.

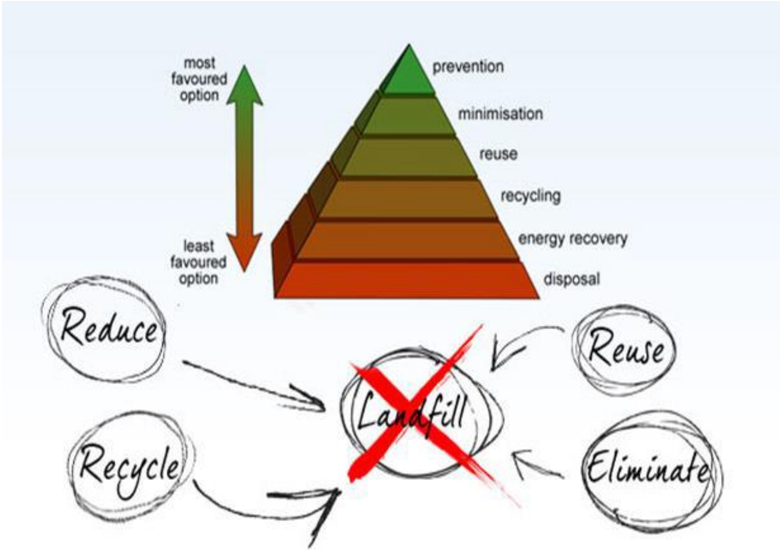

Figure 3. Waste minimisation triangle

Recycling is a method of waste management in the waste minimisation process of the WFD (waste framework directive) waste management heirarchy as shown by the waste triangle in figure 3. Recycling is one of the key ways the UK oil and gas industry can reduce its carbon footprint. Recycling of drilling fluids is a way of minimising waste to the environment via landfill sites to groundwater system, land, flora and fauna [6]. It is carried out to ensure that waste drilling mud can be converted into other products for further use. Technically, there are two kinds of recycling: Closed loop and Open loop recycling [5].

Recycling of drilling fluid ensures the safe use of drilling fluid as product from 'cradle to cradle' rather than 'cradle to grave' which discourages and minimises the use of the landfill disposal option. As common practise in waste management, the waste have to be sorted, separated, and treated for impurity removal before recycling. The raw waste material, spent (used) drilling fluid is sorted to remove most drill cutting, then, the waste is separated into oil, clean water and solid by phase separation treatment and could be modification before it can be reutilised. This work aims at recycling this oil and gas waste to an essential commodity, a want – a nanofiller for the Nanocomposite material industry.

1.2 Nanocomposite

Nanocomposite material is a unique of material made up of a synergy of different materials such as polymers (biological or synthetic), nanofillers, and metals. Nanocomposites are vital in today's world of sustainable innovations. Thus, the wide variety of engineered nanocomposite materials available for use today from metallic to plastic based nanocomposite materials. They offer high performance, cheaply fabricated and sustainable materials for different applications for construction, tool, household materials and more [12].

1.2.1 Nanofillers: These are materials added to polymers and distributed within the matrix of the polymer to produce a nanocomposite. They are used in the composite industry to enhance and modify the state of different polymeric materials and thus, improve performance, functionality, value, efficacy, benefits, reduce cost and effectiveness of the polymer product [11]. Some of the properties that can be improved or controlled include: mechanical properties, rheology, transparency, flame retardant, electro conductivity or magnetism. Nanofiller may be spherical, flaky, rod-shaped particles. They have a nano dimension of less than 100nm.

In selecting appropriate nanofiller for use, a good understanding and application of the particle size, geometry, chemical modifications or functionality is very vital. Fillers have extensively been used in the production of paints, coatings, sealants, adhesives, concrete, rubbers, and plastics products. Some examples of carbon nanotubes, clay (layered silicates), calcium carbonate, magnesium hydroxide, silicon oxide, glass nano fibers, metallic nanoparticles, grapheme, barium sulphate [13].

1.2.2 Polymer

The polymer of interest in this work is Polyamide 6. Polyamide 6 (PA6) is also called Nylon 6. Gorrasi et al, 2002 used a combination of PA6 and montmorillonite (clay nanofiller) to produce nanocoposites and study nanofiller-polymer interaction. The choice of PA6 is for two reasons: its high temperatures of melting/decomposition and its thermoplastic nature which encourages further recycling. It has a density of 1.15g/cm^3, melting point / glass transition of >220^{o}C and thermal degradation temperature of >300^{o}C. It is tough, elastic and lustre. It is wrinkle free, resistant to abrasion, chemicals sua10^{13}/10^{10}Ohm h as dilute acids and alkalis. It could have a high tensile strength of 3000/1000MPa, elongation at break of 70/200%, Stress at yield of 80/45MPa. It could have a dielectric constant at 1MHz and 50Hz at 3.5/70 and 4.0/12/0 respectively. The dissipation factor at 50 Hz and 1MHz is 100/300 1 E-4 and 310/3000 1E-4.Dielectric strength is 15kV/mm. the thickness of its electrical strength is 1.0mm while Volume and surface resistivity are 10^{13}/10^{10}Ohm.m and 1013/1010 Ohm. Thermal: conductance is 0.23W/Km; while linear thermal expansion along cross to the direction of flow is 70/10 (10-6/K) [14]. PA6 finds application in the automotive and building industries.

2. Materials and methods

Polyamide 6 was obtained for the plastic shop. Spent oil based drilling fluid was donated by oil and gas company, Aberdeen, UK. SEM/EDXA experiment was carried out using Zeiss EVO LS10 variable pressure scanning electron microscope/energy dispersive x-ray. Perkin Elmer ICPOES was used to carry out the metal analyses. Smear test using plain white paper was carried out to ascertain oil free nature of the treated solid (drilling mud). Particle size analysis was carried using the Malvern particle sizer.

3. Results and Discussion

3.1 Influence of nanofiller geometry

Bentonite clay is in the montmorillonite which are known as layered sillicates. Their nature enables them to disperse into separate layers as shown in the SEM image in figure 4. These layers have gaps between them called interlayer spaces or gallery. These spaces allow for ion exchange with organic and inorganic cations which can alter the spaces. The spaces also allow for the satisfactory interphase adhesion between the polymer with filler which could occur in three forms: (i) Intercalated nanocomposites; (ii) intercalated, flocculated nanocomposites and (iii) exfoliated nanocoposite)as shown in figure 5. Clay fillers could contain sodium, potassium, aluminium and magnesium ions which accounts for their hydrophilic nature. Thus, best interaction with this kind of fillers will be the hydrophilic polymers [15]. For better interaction with hydrophobic polymers the fillers are treated with organophilic or hydrophobic tailed surfactants with cation surfactant treatment to reduce surface energy of silicate, increase layer spaces and raise the fillers wettability by the polymer. Studies by [4] showed that PA6 combination with clay could result in exfoliated nanocomposite. Furthermore studies by Cho and Paul, 2001, and Fornes et al 2002 signifies that surfactant treatment could enhance dispersion of clay matrix of the filler and enhance clay polymer interaction [7,8].

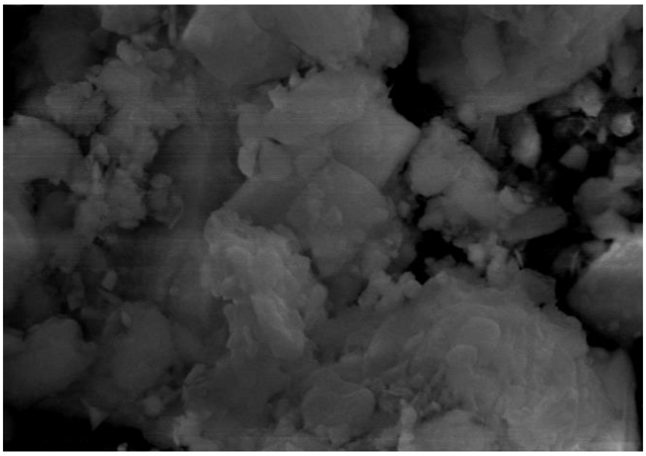

Figure 4. SEM image of Treated (Oil-free) spent oil based drilling fluid (2μm, Mag = 13.18K X)

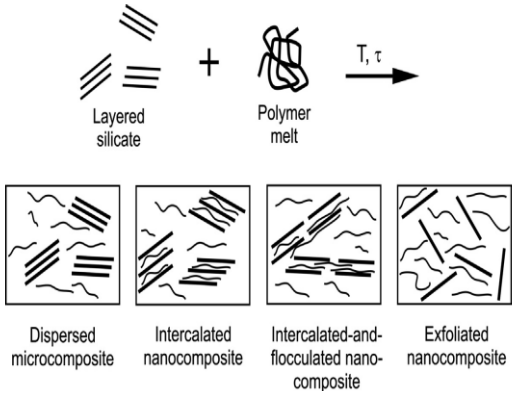

Figure 5. Types of nanofiller – polymer interaction.[15]

3.2 Effect of filler

Information on the MSDS of the formulated oil based drilling fluid from the manufacturer indicates that it contains bentonite clay and barite as weighting agents, and the main solid content. Some other drilling fluid may contain other weighting agents and solids such as Calcium carbonate, Hematite. During the drilling process, as the drill bits crushes the formation the drilling fluid carries the drill cutting of various sizes to the surface to be removed from the drilling mud. However, some of the cuttings are crushed into very fine particles which cannot be removed by the shale shaker. Thus these very fine cuttings (about 0.02 um) are collected as part of the spent oil based drilling mud (drilling fluid) for disposal. Depending on the drilled formation, the fine size cuttings may be from sand stones or lime stone, hence, increasing the concentration of silicate or calcium/carbonate respectively in the spent drilling mud. Nanoclay introduction through reinforcement with 5 wt% Claytone in polymer nanocomposite manufacture improved the optical transparency, mechanical and thermal properties [9].

3.3 EDXA elemental composition of proposed nanofiller

Energy dispersive x-ray analysis (EDXA) was carried out to ascertain the elemental composition of the treated oil based drilling fluid. The result shown in figure 6 indicates that the nanofiller contained Na,Ca, Al, Mg and Mn were attributed to have come from the ion exchange surface of the clay. Si was inferred to arise from the silicate matrix of the bentonite clay used in the formulation of the drilling mud (fluid). Fe was suggested to have come from oil and gas piping, Ba was inferred to be arising from the Barium sulphate weighting agent added to the drilling fluid during formulation. C, carbon and O, Oxygen were expected to have arisen from the organic, eco-sustainable biodegradable cleaning agent used to extract or remove the oil (petroleum hydrocarbon) from the drilling mud solid. Cl was attributed to have been contributed from the sea water NaCl used as wash water or electrolyte additive in cleaning agent.

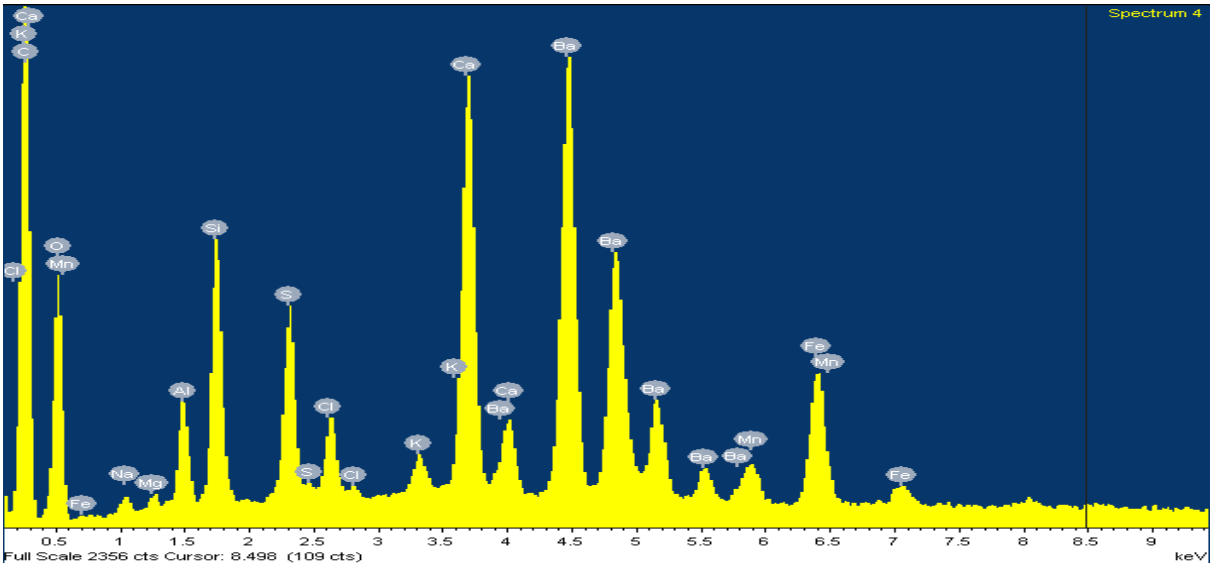

Figure 6. EDXA graph of spent oil based drilling mud

3.4 Particle size of the spent drilling fluid solid for nanocomposite manufacture

Particle size analysis report showed that about 0.33-0.40% of the sample were under 100nm. This was attributed to improperly dispersed solids after oil extraction and drying. Thus, for use of the treated oil based drilling mud waste solids as nanofiller, they would have to be pre-granulated before use as nanofiller in order to get a fine dispersion of the filler within the polymer matrix, produce a fine textured nanocomposite material and most importantly for the nanofiller particle size to qualify as a nanoparticle. A second alternative would be to treat and dry the treated drilling mud in such a way as to prevent the formation of solid lumps.

3.5 Heavy metal content of untreated spent (used) oil based drilling fluids

Due to the health concerns regarding the heavy metals likely to be present in the untreated drilling fluid, it was important to carry out a proper quanitative metal analysis to find out the metal concentration in the untreated nanofiller. The information would enable researchers justify the possibilities of using the nanofiller without treatment without possibilities of environmental harm arising, or the importance for the cleaning treatment agent to wash off, extract or remove the heavy metals present to as low as practicably possible. Currently, the heavy metal concentration of treated drilling mud is not reported. Table 1 gives the concentration of the heavy metal in the untreated oil based drilling mud sample. The information in Table 1 would enable treatment formulator and synthesisers to establish the content of treatment (oil/heavy metal removal agent) required for appropriate metal extraction, and the number of washes required to reduce heavy metal concentration to as low as practically possible, the kind of polymer to used in the production of nanocomposite material and finally, specific application of the nanocomposite material. Other metals and elements analysed by the ICPOES include: Ba (20448 mg/kg), Ca (2122mg/kg), Na (437.6mg/kg), Mg (238.43mg/kg), Mn (94.38mg/kg), Al (877.12mg/kg), Fe (1561.82mg/kg), k(136.74mg/kg), Sr (26.75mg/kg) Si (14.86mg/kg) and S (625.23mg/kg)

Table 1. Heavy metal concentration (mg/kg) of the untreated oil based drilling mud.

Heavy Metals	Concentration (mg/kg)
As	0
Cd	0
Cr	2.87
Cu	5.08
Ni	1.62
Zn	20.18
Hg	0
Pb	30.44

3.6 Possible applications

The high mechanical strength of PA6 (nylon 6) has ensured its utility for making different durable materials such as strings for musical instruments for instance guitar and violin. It is also used in making brushes and adhesives. It is used in packaging and clothing. According to [16] Toyota Japan has used it for the manufacture of auto parts such as the body. Other auto parts include dashboard, oil and water tanks. It is used in car parts as a result of its high melting point. The aim of this work is to recycle the treated oil-free drilling mud into a nanocomposite material for use in the oil and gas and automotive industries. By adopting this process, it is expected that unremoved heavy metals can be entrapped/ engulfed inside the naocomposite material. This process could be seen as a solidification and stabilisation method for the remaining (unextracted) heavy metals. The research findings and analytical results in this work suggests that the nanocomposite material of PA6 and treated oil based mud could be used to make pipelines, oil and gas pipeline (pipe-in-pine application), corrosion inhibition pipe liners, seals, rig floor and wall structure and, unexposed automotive parts such as oil tanks. These applications were chosen so as to prevent the reach of vulnerable people.

4. Conclusion

There is a real potential for recovered and treated solids from spent oil based drilling fluids to be recycled as a nanoclay fillers and used in the production of engineering nanocomposites materials. This application would certainly promote the European waste framework directive by diverting the recovered drilled solid from landfill sites to manufacturing plants for the manufacture and production of nanocomposite materials. It could be used to save money spent on the purchase of resins and other expensive materials used as nanofillers for engineered nanocomposite materials. Our future work entails analyses on the performance characteristics of nanocomposite materials produced from PA6 and the treated waste drilling mud nanofillers as well as working out a policy and advocacy framework for the full adoption of spent drilling mud waste as nanofillers.

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