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3D Printing High Performance Polymers and the Oil and Gas Industry

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ABSTRACT

Additive manufacturing and 3D printing hold a number of promise in bringing on-demand and high-performance parts production capable of adding high value to the oil and gas industry. Non-metallic parts offer a number of advantages in reducing corrosion issues and enabling properties such as high-temperature resistance or reversibly, dissolvable or degradable properties. However, most parts used for completion and down-hole tools are still based on traditional molding, extrusion, thermoforming, etc. methods. 3D printing methods (FDM, SLA, SLA, VSP, etc.) holds promise in fabricating parts ranging from high-performance polymer materials (PEEK, PPS, Ultem, etc.) to elastomeric (thermoset elastomer and thermoplastic elastomer) materials. The use of polymer nanocomposite polymers is also a possibility. This talk will give an overview of 3D printing polymer materials from high-performance polymers, elastomers, and nanocomposite materials with high potential for the industry and current projects in the Advincula Research group. This will also enumerate their testing for thermo-mechanical properties including possible new protocols for evaluating performance for downhole conditions, environmental exposure, and degradation properties.

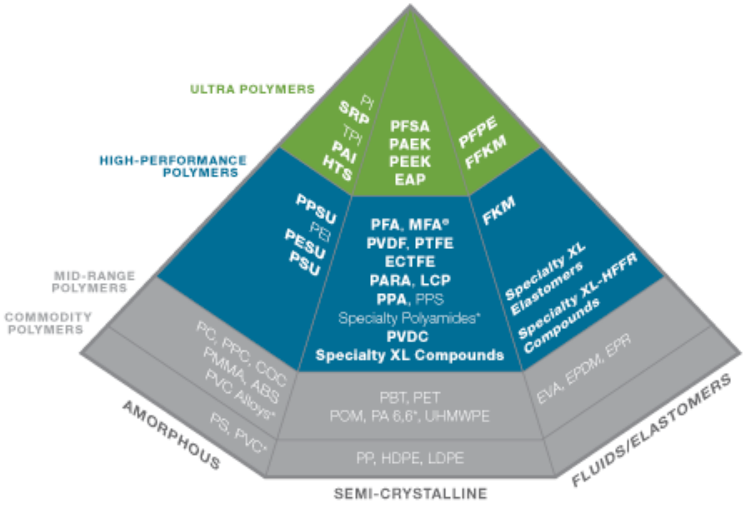
Key words: coatings, anti-microbial, anti-corrosion, oil and water separation.

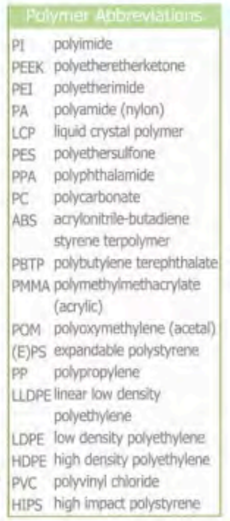
INTRODUCTION

Oil/gas upstream exploration and production is one of the most important extractable natural resource for fuel, energy, chemicals, and materials generation. Metals, plastics and other materials industries, owe much of its feedstock from oil/gas and petroleum (e.g., ethylene to produce polyethylene) either as an energy source for running the plants or as raw materials. Extraction of this resource requires new technology and materials that for highly demanding environments in terms of thermo-mechanical properties, anti-corrosion properties, chemical stability, ductility, etc. Sometimes, it is even desirable for these properties to degrade over time or instantaneously (resorbable or dissolvable polymers).

Downhole tools, completions tools, packers, sensors, and instruments exposed to the resource environment demand that they perform in various environments including higher pressures and higher temperatures. This includes repeated use of these tools for various exploration and production operations. Prior to production, a well needs to be completed. During the completion stage tools are needed for staging, isolation, retrieval, well direction and setting, etc.. This includes packers, seals, retrievable packers, cement retainers, bridge plugs, selective treating tools, setting tools, etc. A number of them are meant to work not only under higher pressure and temperatures (HPHT)s but also under flowing cement or high brine conditions. Once the completion stage is finished, the production mode is ushered. The proper design of this "completion string" is essential to ensure the well can flow properly on specific reservoir conditions and permit operations necessary for enhanced and long-term production. For production, parts of this include the: wellhead, blowout preventers or Christmas tree, tubing hanger, production tubing, downhole and annular safety valves, mandrels, submersible pumps, packers, perforating joints, etc. While a good number of these parts and tools are made of metal and corrosion resistant alloys, *increasingly they have components made up of polymer based materials* (thermosets, rubbers, elastomers, and thermoplastics) and are classified as corrosion-free components. It is of high interest to develop the non-metallic equivalent and more importantly explore the potential of additive manufacturing (AM) to develop these replacements.

For the oil and gas industry, the time-to-delivery of new tools, parts, and equipment through better designs and combining of parts are advantageous, i.e. parts made separately by injection molding, casting, thermo-forming, extrusion, etc. need new paradigms. AM or 3D printing is a promising method for manufacturing and fabrication, beyond just prototyping. This is in contrast to the conventional formative manufacturing (molding, extrusion, thermoforming, etc.) and subtractive manufacturing, which requires removal of materials to achieve the desired net shape. By volume, compared to metal AM, the non-metal (polymers) AM (ceramics are the other materials) comprises the largest volume of AM fabricated parts and objects. This can be divided mostly between, thermoplastics, thermoplastic composites, thermosets, and elastomers. They can also be classified as commodity polymers, engineering polymers, and high performance polymers (Figure 1). The price per unit weight goes higher with increasing performance (tensile strength, chemical resistances, heat deflection temperatures, etc.)[1] Methods for employing polymer thermosets and elastomers for AM are just emerging. The need to improve their performance/properties is key to growing their uses in oil/gas industry applications.

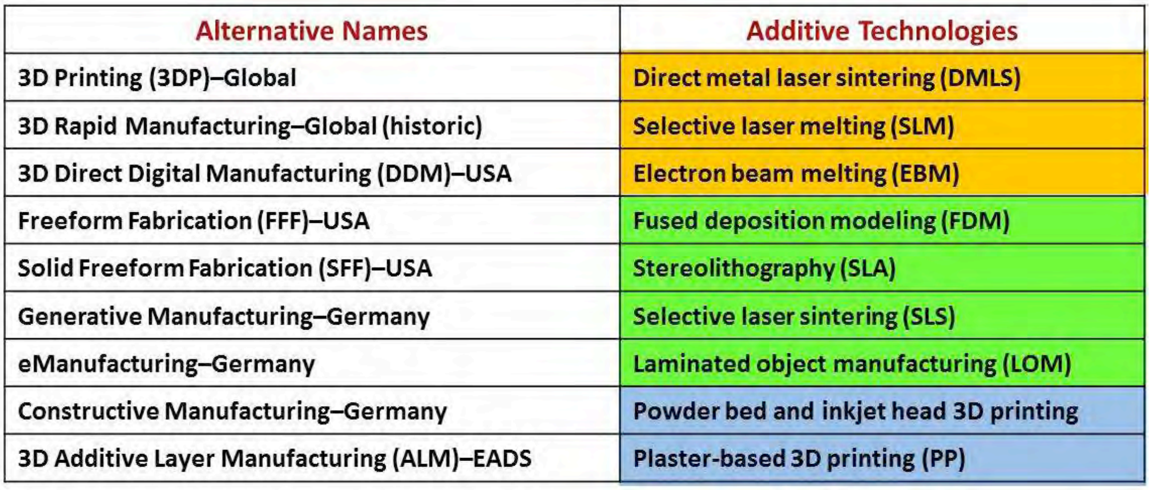




Polymer Abbreviations	
PI	polyimide
PEEK	polyetheretherketone
PEI	polyetherimide
PA	polyamide (nylon)
LCP	liquid crystal polymer
PES	polyethersulfone
PPA	polyphthalamide
PC	polycarbonate
ABS	acrylonitrile-butadiene styrene terpolymer
PBTP	polybutylene terephthalate
PMMA	polymethylmethacrylate (acrylic)
POM	polyoxymethylene (acetal)
(E)PS	expandable polystyrene
PP	polypropylene
LLDPE	linear low density polyethylene
LDPE	low density polyethylene
HDPE	high density polyethylene
PVC	polyvinyl chloride
HIPS	high impact polystyrene

Figure 1: Hierarchy of polymer materials and their performance including commodity polymers.

AM or 3D printing for oil and gas is characterized with the stages of: 1) CAD design or digital scanning/imaging. 2) Surface Tessellation Language (.stl) file conversion - means that objects or parts will be built up one layer at a time on an X-Y substrate plane surface and added on top of each other on a Z direction. 3) G-code specification – optimized parameters to define the best printing or desired output and is printer specific, 4) actual printing, and 5) post-curing or finishing. Various technologies have been introduced in the field of AM, such as; stereolithography (SLA) using liquid resin photocuring processes, selective laser sintering (SLS) which involves sintering of layer-by-layer powdered materials, selective laser melting (SLM) involving polymer powder and laser beam-based manufacturing process, fused deposition modeling (FDM) involving deposition of melt extruded layers of material through a nozzle using a feedstock filament, liquid deposition modeling (LDM) involving deposition of polymers using a solvent, etc. (Figure 2). The advantage of AM is in creating more complex object geometries and multi-compositions not easily achieved with traditional subtractive manufacturing (i.e. CNC milling) due to the difficulty of removing bulk monolith material internally and precisely or without support materials. By reducing the design-manufacturing cycle, AM provides the possibility of reducing the production cost and increasing the effectiveness of manufacturing and on-demand production basis.



Alternative Names	Additive Technologies
3D Printing (3DP)–Global	Direct metal laser sintering (DMLS)
3D Rapid Manufacturing–Global (historic)	Selective laser melting (SLM)
3D Direct Digital Manufacturing (DDM)–USA	Electron beam melting (EBM)
Freeform Fabrication (FFF)–USA	Fused deposition modeling (FDM)
Solid Freeform Fabrication (SFF)–USA	Stereolithography (SLA)
Generative Manufacturing–Germany	Selective laser sintering (SLS)
eManufacturing–Germany	Laminated object manufacturing (LOM)
Constructive Manufacturing–Germany	Powder bed and inkjet head 3D printing
3D Additive Layer Manufacturing (ALM)–EADS	Plaster-based 3D printing (PP)

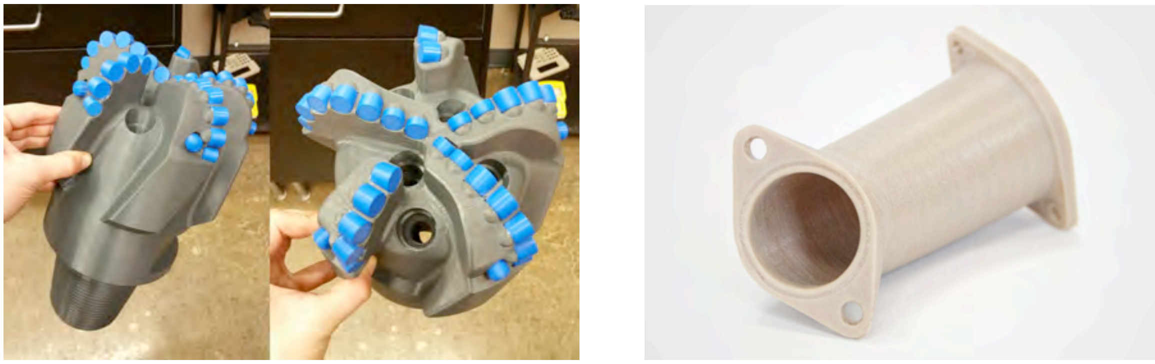


Figure 2: List of 3D Printing and AM Methods commonly used and their classifications based on the type of materials or form use for fabrication. This includes examples of proto-type design and materials (figures from reference 6).

In this paper, we present an overview of materials and trends related to 3D printing of polymers, high performance polymers (HPP)s, and nanocomposite polymers – their use and the advances in AM methods. In particular, we emphasize the potential of these materials used in AM and its possible applications in Oil and gas. Then we also present some of our own results on these studies utilizing nanocomposite materials and combinations of materials and processing conditions in solution or melt. In particular, our studies include: 1) FDM Printing of polyurethanes with enhanced thermo-mechanical properties and use of graphene, 2) SLA of photopolymerizable resins including silicone and cellulose nanocrystals (CNC), 3) SLS fabrication of polyamide composites, and 4) nanocomposite polyetheretherketone (PEEK) and polyphenylene sulfide (PPS) materials containing POSS nanomaterials and blends with other polymers such as nylons.

EXPERIMENTAL

Methods and Materials:

The methods and materials preparation described here are general conditions ascribed in AM. More details can be found in the corresponding original papers.[2-5] In general, polymer materials are prepared as filaments, photopolymerizable resins, powder-based materials and viscous paste inks. These comprised of polyurethanes and thermoplastic polyurethanes (TPU), polyamides or nylon12 materials, silicone adhesive and silicone telechelics, the acrylate monomers/solution used in photopolymerization was prepared by mixing the monomer, initiators, crosslinkers, and solvent, and eventual removal of solvents. Filaments are prepared by solution and melt blending over several cycles to observe homogeneous cycles. The PPS filaments were prepared at the desire filament diameter and lengths necessary for object fabrication. Powders are prepared by powder mixing and milling to ensure homogeneous powder dispersions. Pastes and viscous inks were mixed with centrifugal mixers to ensure homogeneous mixing with the proper viscosity. The protocols for nanocomposite preparation with graphene (graphene oxide- GO), Polyhedral Oligomeric Silsesquioxane (POSS), and nanoclays for filaments, resins, and powders are described in the corresponding reference and papers.

General Instrumentation

Again, the general description of instrumentation and 3D-printing methods provides a partial list and function of the instrumentation and fabrication methods used in the experiments and more details are found in the references. [2-5] FDM was performed using a combination of printers which enable effective loading of the Filament and the right temperature head for the specific polymer (Ultimaker, Gigabot from re:3D, Intamsys “high temperature printer” and Raise3D). SLS was performed using the Sintratec SLS printer, SLA photo polymerization printing was performed using the Formlabs 3 or the Photocentric DLP printer, and Viscous solution printing (VSP) was done using the Stuctur3D attached to an Ultimaker or the Hyrel Printer. Scanning electron microscopy (SEM) analysis of morphology was done using JEOL SEM instrument. The ATR IR spectroscopy was done with Cary 600 Series FT-IR spectrometer was used with scanning range of 400-4000 cm-1 (Agilent Technologies). UV-Vis spectra were obtained by using an Agilent 8453 spectrometer. The thermal stability of the monomer and the polymer was measured using a TGA 2050 thermogravimetric analyzer to monitor weight loss or determine composition. Rheological properties were measured using Mars III rheometer (ThermoFisher Scientific, HAAKE). For thermo-mechanical testing, an MTS Universal Testing Machine (UTM) with a 5 kN load cell was used. ASTM D638 was adopted for the tensile tests and a minimum of 3 samples were always tested. The same UTM used for the tension tests was used for the compression tests. ASTM D695 was adopted for the compression test and 3 samples were tested.

DISCUSSION AND RESULTS

Oilfield service companies and oil/gas operators have important logistical challenges, due to wide geographical distribution of operations. The high cost of downtime presents very real parts and supply logistical challenges. The timely delivery of parts for maintenance and repairs is vital. Operators strive to minimize unscheduled downtime by maintaining large inventories of critical spare parts. AM can optimize asset maintenance by enabling faster repairs and improving design quality for high performance. With on-demand 3D printing it can minimize inventories of spare parts and dramatically improve supply chain management.

3D printable polymers can be classified based on their temperature, chemical, and mechanical stability. Polymers can be classified as standard polymers, engineering polymers, or high performance polymers (HPP). For convenience, we can classify polymers used for oil and gas based on their temperature rating. Standard polymers, also known as commodity polymers, are polymers that have low mechanical properties and can only be used at temperatures <100 ^{o}C. Examples are polystyrene (PS), polyvinyl chloride (PVC), polypropylene (PP), and polyethylene (PE). They are produced in large volume and are used in a wide range of low-temperature applications hoses, coatings, surface and derrick parts, etc. and other applications where mechanical properties are not too critical. To date the most common 3D printed commodity polymers such as polylactic acid (PLA), acrylate-butadiene-styrene (ABS) are unsuitable for field operations. Engineering polymers are polymers with better mechanical and thermal properties than standard polymers, and can be used at temperatures between 100 - 150 ^{o}C. They are used in low-volume applications because of cost. Examples of engineering polymers are polyesters, polycarbonates (PC), and polyamides (PA). Applications of engineering polymers include structural parts, knobs, seals, links, coatings, to list a few are not suitable for field applications. Other types polymers are included as elastomers and thermosets can be described as epoxys and rubbers have a better prospect. Epoxy, novalac, and polyurethane thermosets, are usually observed as toughened or high-hardness (high density parts) and corrosion resistant. The use of hydrogenated poly(polybutadiene-acrylonitrile) HNBRs (nitrile rubbers) for packers are well known. However, the higher build volume 3D printing strategies of these thermoset and thermoset elastomers are still being developed. HPPs, on the other hand, are polymers that meet higher requirements than standard and engineering polymers. They can operate at temperature > 150 ^{o}C. They are characterized by superior mechanical properties, outstanding chemical stability, and exceptional thermal stability. Examples of HPPs include amorphous polymers: polysulfone (PSU), polyetherimide (PEI), semi-crystalline polymers: polyphenylene sulfide (PPS), polyetheretherketone (PEEK), and various liquid crystalline polymers (LCP)s. They can withstand and retain desirable properties at harsher conditions such as corrosive environments and HPHTs. They have been termed as high temperature polymers, advanced engineering materials, and heat resistant polymers. The interest in developing 3D printable HPPs for the oil and gas industries is driven by the need to have materials with outstanding mechanical, dimensional, and chemical stability that can survive high temperatures and pressure and more extreme environments including downhole conditions.

Other than demonstrating the feasibility of printing parts for prototyping, the need for testing demand the modifications of current ASTM, API, NACE and ISO standards to differentiate anisotropic properties of 3D printed parts with conventional monolith formative or subtractive manufacturing. This includes tensile strength, flexural strength, compressive strength, shore hardness, humidity effect, oil/hydrocarbon wetting, corrosion and scaling environments (pH and brine conditions), etc. Important thermo-mechanical testing methods for AM parts were recently outlined in our review paper.[1]

Our research into 3D printing methods and new AM materials. The general protocol for preparing the 3D printing materials is found in the respective references of our previous: filaments, powders, photopolymerizable resins, and viscous pastes. The instrumentation and testing methods are described in general on the experimental section in the corresponding references. A number of strategies for functional and nanostructured 3D printed materials are summarized below, primarily as a demonstration of the possibility of 3D printing and possible uses of the materials based on the general classification of the polymers used. This was demonstrated in the following systems:

1. *High Performance Thermoplastic Polyurethane with Graphene via FDM.*[2] We have successfully 3D printed thermoplastic polyurethane/polylactic acid/ graphene oxide (TPU/PLA/GO) nanocomposites by using a solvent mixing process as well as the FDM technique. (Figure 3) Nanocomposites can be easily printed in to complex shapes with high quality. FTIR and SEM images revealed good dispersion of graphene oxide (GO) in polymer matrix. The addition of GO significantly enhanced the mechanical properties of the polymer matrix, 167% in compression modulus and 75.5% in tensile modulus. The printing orientation led to different mechanical responses due to the weak adhesion strength between layers during 3D printing. Thermal stability was improved, > 90 °C increase in degradation temperature as well as formation of better crystalline structures. Based on our results, the 3D printed TPU/PLA/GO nanocomposite exhibited excellent mechanical properties, thermal stabilities which will allow it to be widely applied where current TPU applications in the oil/gas industry exists. Some examples include:

tubes, bushings, rings, nozzles, scrapers, clamps, seals, gears, liners, pads—polyurethane can possibly 3D printed into any of them, with custom additions if needed.

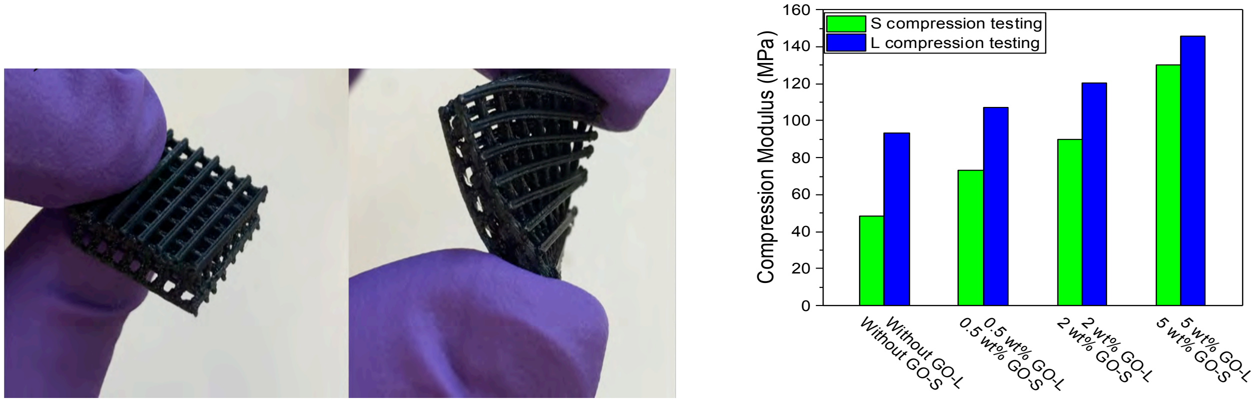


Figure 3: 3D Printed Polyurethane/PLA/GO nanocomposites showing elastomeric properties and black color (due to GO). The addition of GO improves the compression modulus and in-general exhibit anisotropic properties based on the printing direction (ref. 2).

2) *Polyacrylate Resins with Graphene via SLA.*[3] A process for strengthening SLA-printed polyacrylate-graphene oxide (GO) nanocomposites has been reported. This makes use of GO's metastable structure through mild annealing after 3D printing. Modulus and tensile strength decreased for both the Control and samples annealed at 50 °C. In contrast, samples annealed at 100 °C experienced a drastic increase in mechanical properties and thermal stability with the highest % increase recorded at 673.6% for the 1 wt% GO nanocomposite. This enhancement was attributed to three reasons: (1) removal of intercalated water in the GO membranes, (2) removal of labile oxygen-containing groups on the edges of GO, and (3) decrease in pore size of the resin with increasing annealing temperature. The results were confirmed by XRD, FTIR, and SEM, respectively (see publication). Furthermore, TGA and DSC data showed enhancement of thermal behavior with increasing annealing temperature. It was demonstrated that its properties are comparable to traditionally casted parts of the same material annealed at 100 °C. This study may be extended by further annealing at temperatures high enough to induce reduction of GO to graphene, giving the resulting parts better electrical and thermal conductivity properties. While SLA and use of acrylates are considered as weak materials for oil/gas, their contribution is in producing the highest resolution for current 3D printed parts. Therefore it will be important to further strengthen their thermo-mechanical properties and improve their chemical/environment stability where high-resolution print parts are eventually needed (sensor housing, arrayed or miniaturized parts in downhole instruments, more complex geometries, etc.)

3) *Thermal and electrically conducting nylon composites via SLS 3D Printing.*[3] 3D-printed carbon black/polyamide-12(CB/PA12) parts via SLS with various wt.% carbon black loading was investigated in terms of consistency of carbon black and PA12 content, improvement and degradation in tensile and compressive strengths, and thermal stability. The electrical percolation occurred between 1.5 wt.% and 3 wt.% carbon black. The bulk resistivity measurements showed consistent carbon black content in each sintered sample. When compared to the sintered neat polymer, the tensile and compressive strengths achieved four-fold and five-fold improvement with the 1.5 wt.% carbon black loading, and a 33% improvement with 3 wt.% carbon black. On the other hand, adding more than 5 wt.% of carbon black produced significantly lower tensile and compressive strengths compared to the sintered neat PA12. This was attributed to the surface crowding of PA12 particles by carbon black, that hindered the physical contact between PA12 particles, which is a key parameter to effective sintering. The maximum degradation temperature of all CB/PA12sintered parts was higher than that of pure PA12 due to the higher thermal properties of carbon black particles, which contributed to the overall higher thermal

stability of the sintered parts. The 1.5 wt.% CB/PA12 sintered part has shown the most improvement in terms of mechanical properties without compromising the electrical conductivity capability and thermal stability. The full results of this work will be reported in a full publication.[4] Possible application of these work will be in substituting nylon based parts requiring better thermal and electrical conductivity (or shielding) in a more complex design (sensor housing replacement, field jigs and tools for repair, safety tools, etc.)

4) *3D printing PEEK-POSS and PPS-POSS Nanocomposites*. Lastly, we have investigated the FDM 3D printing of PEEK–POSS blended filaments and possible improvements on thermo-mechanical properties at high temperatures (Figure 4). The addition of POSS enables the development of better resistance again stress crack propagation. However, nanostructuring and homogeneous dispersion of additives is important for attaining the proper percolation threshold. The PEEK-POSS filaments were prepared by melt blending up to 3% of PEEK with POSS nanomaterials. The filaments were prepared by single-screw extrusion methods and were cycled up to 3 times to ensure thorough mixing of materials. The filaments were then developed based on the die head diameter of 2 to 3 mm and the appropriate lengths to enable fabrication of the dogbone and box structures suitable for thermo-mechanical testing. For thermo-mechanical testing, an MTS Universal Testing Machine (UTM) with a 5 kN load cell was used. ASTM D638 was adopted for the tensile tests and 3 samples were tested. The same UTM used for the tension tests was used for the compression tests. ASTM D695 was adopted for the compression test and 3 samples were tested. Results show a slight improvement in tensile strength with 3% addition of POSS. However it is necessary to investigate higher loadings of nanomaterials. Compression tests will be done in the near future and full reporting in a publication including results from PPS-POSS fabrication and testing.[5]

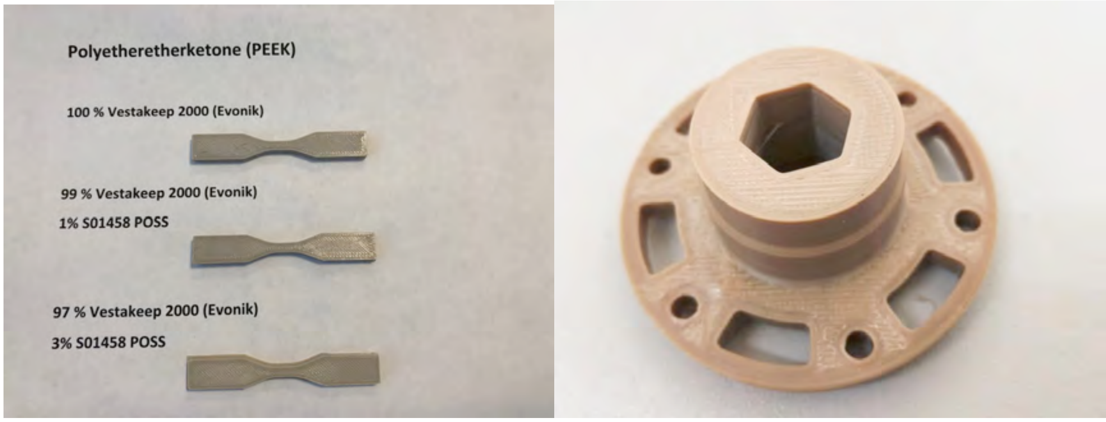


Figure 4: 3D Printed PEEK-POSS dogbones and a sample part showing the quality of print and the potential properties that may be tested (tensile, compression, flexural, shore hardness, etc.) The addition of POSS nanocomposites improves the anisotropic properties based on the printing direction. Additional post-curing procedures will be investigated.

CONCLUSIONS

In this paper, we have outlined the potential uses and advantages of 3D printing in the oil and gas industry. The general classes of AM and the protocol for preparing the 3D printing materials can be related to various classes of polymer materials: from commodity polymers to HPPs and their advantages in terms of cost/performance. A number of strategies for functional and nanocomposite 3D printed materials are reported from our group - primarily as a demonstration of the possibility of 3D printing and substitution of current materials for oil and gas (upstream applications). This includes: a) a higher performance TPU by FDM, 2) improved acrylate-graphene composition via SLA, 3) improved thermal and electrical conductivity with nylon-12/carbon black composite via SLS, and 4) FDM printed PEEK-POSS composite with better thermo-mechanical properties.

To summarize the main reasons for developing AM for the industry:

1. *Reduced downtime.* Downtime in the oil and gas industry is very expensive, particularly on remote and/or offshore rigs. AM has the potential to limit downtime through reduced lead times and supply chain enhancements. The prospect of on-site manufacturing and parts replacement becomes more viable with AM. Many components on drilling rigs include multiple parts that must be welded, bolted or brazed together. The 3D printing of single-piece designs at remote locations could significantly reduce costs and downtime (parts need not be transported into remote locations and the stocking of combined or fused parts).

2. *Direct input on design and manufacturing.* 3D printing innovation in the oil and gas industry, will benefit on the input from the field staff observations and experience. This can be as simple as identifying parts/ components with high exposure or breakdown. However, to maintain rigorous performance and safety standards, industry certification of 3D printing materials and parts needs to be developed.

3. *Fast prototyping of parts or limited production.* An important current benefit of 3D printing is already demonstrated in rapid prototyping where oilfield companies are able to develop and validate their designs faster, thereby accelerating the design process and addressing performance and operation issues – giving a technology cycle edge for early adaptors. Rapid prototyping allows the oilfield service companies to engage in less multiple design cycles and quickly test design concepts in real time or go to limited production.

4. *Integrated design and complex geometries and materials.* The oil and gas industry uses complex parts and tools that must meet robust performance and environmental standards. Higher pressures, higher temperatures, exposure to brine conditions, scaling, corrosion, etc. are not uncommon. AM allows for innovative shapes, complex geometries, and batter materials that reduce the number of parts. Compared to stock parts, AM allows for application specific parts: tools, jigs, pumps, turbomachinery, valves and other vital components specific for the operation which can reduce costs and enhance performance.

5. *On-site and on demand spare parts production.* The oil and gas industry requires many low-volume components that are relatively expensive to manufacture, stock and replace. This is especially onerous in stocking or transporting replacement parts. As the oil and gas industry evolves, improved designs lead to shorter production cycles, e.g. new completion tools, sensors, which only increase the pressure on those responsible for stocking spare parts. In oil and gas, parts availability is key even as the problem of parts obsolescence is inevitable.

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