

Microstructural Characterization, Corrosion and Wear Properties of Graphene Oxide Modified Polymer Coatings for Geothermal Drilling Applications

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ABSTRACT

Polymeric coatings are exploited by adding reinforcements to maximize its industrial performance. The idea of reinforcement is to tailor the matrix's wide-range performance to a specific desired property to prevent component failures. In this work, the polyphenylene sulfide-polytetrafluoroethylene (PPS-PTFE) matrix was modified with graphene oxide (GO) to improve the mechanical properties, corrosion and wear resistance, to provide coatings for drilling components for high-temperature geothermal well environment. Electrochemical test in a 3.5wt% NaCl solution and a pin-on-disc sliding test were performed to determine the corrosion and wear resistance of the novel coatings. The addition of GO reduced the coefficient of friction but increased the roughness and hydrophobic properties of the coatings. The tendency of coatings to minimize corrosion were determined by evaluating the open circuit potential (OCP), corrosion potential (E_{corr}) and corrosion current density (I_{corr}). The coatings showed higher OCP, E_{corr} and lower I_{corr} after 24 hours of immersion. The 1wt% GO polymer coating is the most promising; based on the reduction of I_{corr} of the substrate from 0.15 μA to 0.01 μA and an increased friction and wear resistance by approximately 72%. The results indicate a good coating performance for low GO reinforcement by improvement in surface properties, corrosion and wear resistance.

Keywords: abrasive wear, corrosion, graphene oxide, geothermal, Geo-Drill, hydrophobicity, PPS-PTFE/GO coating.

INTRODUCTION

Geothermal well-drilling and completion of at least 2 km depth are associated with high axial, rotational and vibrational loads. A harsh environment exists for the metallic parts of drill components used across the drill string's length in conjunction with the high-temperature fluid and subsurface differential pressure. The high temperature/high pressure (HT/HP) and the abrasive-corrosive environment in geothermal drilling applications affects the the drilling components including the drill pipes, rod couplings (joint areas), valves, artificial lift systems and the flow assurance in pumping equipment for driving the downhole tools. A typical complication related to low drilling progress is the twist off and loss of drill pipes and the downtime associated with these tools and the subsequent fishing before drilling^{1,2}. These fractures projected through pipe wall thinning or materials loss at couplings and threaded connections results in the enlargement and destabilization at the tool joint. The scale and corrosive species (e.g., Ca^{2+} , Na^+ CO_2 , H_2S , HCl , NH_3) present in the hot geothermal fluid downhole, which reduce into anions (i.e., Cl^- , SO_4^{2-} , S^{2-} OH^- , HCO_3^-), can cause rapid corrosion down-hole³⁻⁵. Material loss or wear is related to friction generated between surface contact coupling from the rigors of drilling or hard abrasive particles from silicate minerals or fractured rocks. When tool joints are attached to the pipe body by roller expansion or welding, coatings are often the tool joints' solution to wear. A high-performance coating with the capacity to withstand high compressive stresses during expansion or thermal decomposition during welding is preferred.

Thermoplastic polymers with ease of application, low-temperature curability, hydrophobic properties, good adherence, and thermal and chemical stability are often used to produce HT/HP anti-scaling, anti-corrosion and wear-resistant coatings⁶⁻⁸. Benzimidazoles, ether sulfones and fluoropolymers have gained popularity for low-temperature curable coating and composites ranging from 25 °C to 80 °C with the thermal stability of up to 300 °C⁶. The present work looks to explore the microstructural, corrosion and wear properties of two engineering polymers: polyphenylene sulfide (PPS) and Polytetrafluoroethylene (PTFE). PPS is considered pivotal for abrasion resistant coatings. The low-cost semi-crystalline polymer is chemically and thermally stable, with a melting temperature of around 275 °C. However, PPS has been found to have an undesirable property caused by sulfite linkage due to oxidation by hot brine. This inherent behavior lead to cracking and loss of coating barrier properties⁹⁻¹¹. Permeable coating results in localized corrosion and delamination due to underlying reactions. An associated problem with oxidation is surface roughening, which contributes to multi-layer scale growth and ultimately affects flow behaviors. Sugama et al.¹¹ proposed a solution to use a superhydrophobic PPS-PTFE blend, which contains a small percentage of the PTFE acting as an anti-oxidant and anti-friction layer, with a secondary composite property of a hydrophobic surface.

Moreover, the addition of nanofillers such as carbon nanotubes, carbon fibers, SiO_2 and Al_2O_3 further improve the thermal and mechanical properties^{12,13}. In this contribution, graphene oxide (GO) with low shear strength is added in small quantities to the PPS-PTFE coating blend to optimize the chemical and mechanical properties for solid lubrication in drilling applications. The PPS-PTFE/GO composites in this study were evaluated for hydrophobicity, anti-corrosion, anti-friction and anti-abrasion performance of the barrier film deposited on carbon steel substrates. This was predicted from laboratory accelerated-electrochemical and dry sliding tests on the coatings. Optical and microscopic techniques were used to analyze the coatings' surface before and after the wear and corrosion tests.

EXPERIMENTAL PROCEDURE

Materials

Three different coatings were applied to standard carbon steel substrates of 30mm disc. The PPS-PTFE blend was mixed with different weight fractions of graphene oxide to fabricate the composite-coatings received from Graphenea SA. A reference carbon steel (CS) and the three coatings were investigated in this study: (a) CS coated with PPS-PTFE, (b) CS coated with PPS-PTFE and 1wt.% GO and (c) CS coated with PPS-PTFE and 2.5wt.% GO. A schematic of the composite produced in this work is illustrated in Figure 1, but the consistency varied within the specific coating composition's cross-sectional features. The rubbing counterpart used for the tribological pin on the disk (PoD) test was a chromium steel (100Cr₆) ball of 6 mm.

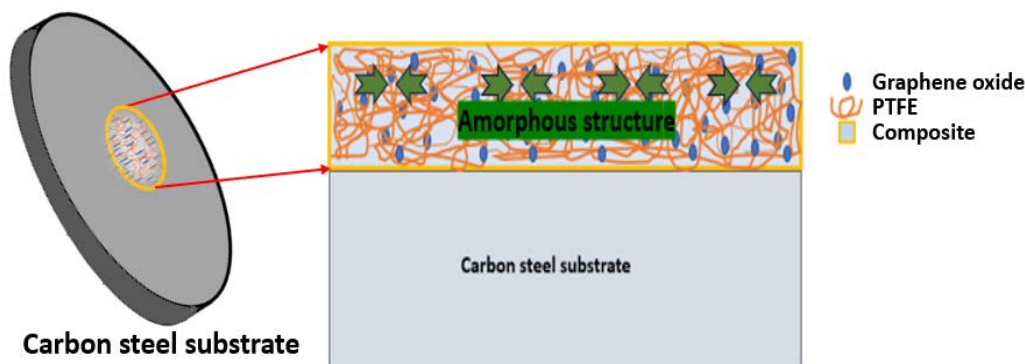


Figure 1. Schematic of PPS-PTFE/GO composite coating on carbon steel substrate material. The GO content varied with 1wt.% and 2.5wt.% for the study.

Material characterization

An optical microscope (Meiji Techno®, Japan) and scanning electron microscopy (FE-SEM, Zeiss Supra 25®) were used to characterize the coatings' microstructure and surface morphology. The elemental composition of the coatings' selected regions was analyzed with an electron dispersive X-ray spectrometer (EDS, Oxford Instruments®, Oxford, UK) attached to the SEM. Roughness measurements were taken to determine topological surface parameters using a Taylor Hobson Ametek stylus profilometer. The measurements and calculations were per DIN/ISO 4287 standard. The static contact angles were measured using a 5 µL drop of water at 15 different locations and the averages recorded to evaluate the coatings' water contact angle (WCA). X-ray diffraction (XRD) patterns were performed using an X' Pert Pro system with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) to determine the crystal structure of additives in the composite coating.

Friction and wear testing

The tribological wear tests of coatings and the carbon steel (CS) substrate were conducted with a ball-on-disc configuration using Anton Paar® TRB³ tribometer. The set-up and measurements followed the ASTM G99 standard. The test involved a 5mm radius unidirectional sliding of a ball pressed on a coated/uncoated disc at an applied load of 5N to generate friction. The test duration and motor speed were kept constant at 3600 sec and 200 rpm, respectively. The coefficient of friction was monitored during rubbing without interruption. The data from the tribometer was expanded with Anton Paar® Instrument X software version 8.1.5. Profilometry images of the surfaces after the test were obtained using Solarius® SD-V100-3219 equipment. The wear rate, w_{sample} ([mm³/Nm]), was calculated by measuring the volume of removed material, V (mm³), correlated to the applied load, F_n (N), and the distance covered during testing, L (m):

$$w_{\text{sample}} = \frac{V}{F_n \cdot L}, [\text{mm}^3/\text{Nm}] \quad (1)$$

Electrochemical corrosion testing

For electrochemical tests, 2.5 cm CS samples disc were ground with SiC grit papers and polished down to 1 μm surface finish using diamond paste. The samples were ultrasonically cleaned in ethanol before immersion in electrolyte for measurements. All the tests were conducted at room temperature. The experiments were carried out using a three-electrode electrochemical cell set-up with saturated Ag/AgCl as a reference and a graphite rod as counter electrode in a solution with 3.5 wt.% NaCl. The corrosion experiments were carried out using a Princeton Applied Research Potentiostat (VersaSTAT 4) with versaSTUDIO electrochemical software (version 2.54). In all cases but the CS, open circuit potential (OCP) measurement was monitored and recorded for 24 hours. Polarization measurements were carried out using a scan rate of 0.167 mVs^{-1} at a potential initiated at -0.5 mV to $+0.5 \text{ mV}$ versus open circuit potential. The results of measured electrochemical potentials were presented vs Ag/AgCl electrode.

RESULTS

Surface morphology, microstructural and chemical compositional analysis

Figure 2 shows SEM micrographs and elemental maps of PPS-PTFE coating and the composite coating of PPS-PTFE with 2.5 wt.% GO. The coatings were amorphous in nature. Fiber-like structures were found on the micrographs' top surface, which is attributed to the semi-crystalline PTFE (C_2F_4). The fibers were engulfed in a porous-rich S matrix. The surface morphology of 0, 1, and 2.5 weight percent was similar. However, at high magnifications, the structures with the addition of GO appeared coarser (see Fig.2b). This is likely due to particle agglomeration and thickening through the GO nanofillers addition and synthesis. At lower magnification, cracks appeared on the micrographs for an increase of GO fraction to 2.5wt%. The cracks are likely caused by air trapping during high-speed mixing of the highly viscous PPS-PTFE blend with an additional fraction of the GO. Table 1 shows the presence of all elements related to the coating from qualitative analysis with the EDS. The corresponding surface elements and coating structures from SEM/EDS maps, the presence of SiO_2 , was observed in all the investigated coatings. There was no conclusive trend for the identified elements, but high S content was observed in all the coatings with F and O. The highest concentration was determined for C, represented with other elements (often Fe and Al) in Table 1. This exclusion of C from Table 1 is due to the limitation of the EDS equipment in detecting smaller atomic elements accurately.

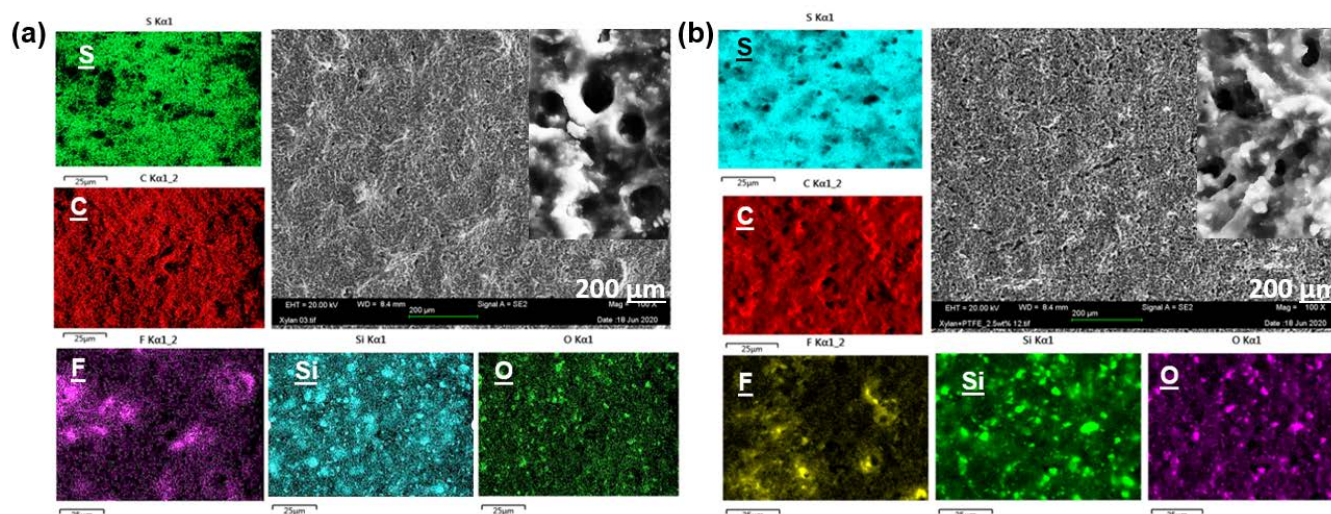


Figure 2. SEM morphologies of surface microstructures (100X and 2.50KX) and elemental mapping of (a) PPS-PTFE and (b) PPS-PTFE /2.5wt%GO

Table 1. Chemical composition in weight percentage of the coatings from EDS analysis.

	PPS-PTFE	PPS-PTFE /1wt%GO	PPS-PTFE /2.5wt%GO
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