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Incorporation of Silica Nanoparticles into the Underlayer of PDA/PTFE
Thin Coatings

An Undergraduate Honors College Thesis
in the

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College of Engineering
University of Arkansas
Fayetteville, AR

by

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ABSTRACT

Polytetrafluoroethylene (PTFE) is one of the most low friction and corrosion resistant solid lubricants. Prior studies have shown that a polydopamine (PDA) underlayer enhances the durability of PTFE thin coating. In this study, 100, 200, and 300 μL of aqueous silica nanoparticle (NP) solutions were added to the PDA deposition solution. The durability and coefficient of friction of PDA/PTFE thin coatings on stainless steel substrates are investigated with and without incorporating the silica NPs. The coatings were tested in dry contact conditions using a Universal Mechanical Tester (UMT) with a ball-on-flat configuration in a reciprocating motion. It was found that the durability of the PDA/PTFE coating are significantly improved when 100 μL of aqueous SiO_2 NP solution were added during the deposition of the PDA underlayer. Formation of transfer film was also observed on the counter face. The significant improvement in the durability is attributed to the increased adhesion of the PTFE coating to the PDA underlayer and the enhanced mechanical strength provided by the NPs as well as the enhanced transfer film on the counterface.

Keywords: Polytetrafluoroethylene (PTFE), Polydopamine (PDA), SiO_2 , thin coating, nanoparticles, friction, wear, durability.

NOTE: This thesis, for the fulfillment of the requirements for the Mechanical Engineering Honors Program, is submitted in a journal paper format.

1. INTRODUCTION

Polytetrafluoroethylene (PTFE) is a polymer extensively studied for its dry lubrication abilities. This polymer can be applied to many applications because of its hydrophobicity, chemical inertness, stability at high temperatures and low sensitivity to humidity [1].

Bulk PTFE has been studied and used widely because of its low friction coefficient [2, 3]. Dhunumalayan et al. in his review paper on PTFE discusses its wide use in both domestic and industrial applications. For example, PTFE is used in ball bearings because it self-lubricates, in implants because it is biocompatible, in chemical industries for filtration because it is chemically inert, and in petrochemical processing because of its stability over a wide range of temperatures [1].

The formation of polymeric transfer films has been shown to be integral to achieving ultralow wear on metal countersurfaces [4]. Harris et al. studied the chemical mechanism of transfer film formation on the wear couple and how this translated to exceptional wear performance of alumina-filled PTFE during reciprocating motion tests. They found PTFE chains, broken during sliding, undergo reactions to produce chain ends which chelate to both the countersurface and the filler particles. The tribochemical reactions involved in the formation of transfer films lead to a polymer-on-polymer system which protect the steel countersurface and provides the ability to withstand thousands of cycles with virtually no wear after an initial run-in period [4].

While PTFE has excellent tribological properties suitable for lubricating the surfaces where rubbing interactions occur, its mechanical properties are not as excellent. As a coating, PTFE can be utilized for its surface properties while maintaining the mechanical properties of the

bulk material. A popular application of PTFE in coating form is as utensil lining. Nonstick pots and pans have a layer of PTFE commonly called Teflon[®]. Two major challenges in creating thin coatings of PTFE are poor coating adhesion and wear resistance. These problems lead to short lifespan of the PTFE coatings. One way found to increase adhesion of PTFE is to create roughness on the substrate surface. Sandblasting and other roughening techniques are used to create an uneven surface for PTFE to adhere to [5].

Other studies have explored primers to increase the adhesion of PTFE. Beckford et al. developed a process using polydopamine (PDA) as an underlayer to attach the PTFE coating to a metal substrate [6]. He found the PDA/PTFE coating could withstand approximately 500 times the rubbing cycles of just PTFE coating. The increase in adhesion was confirmed by scratch test results. His findings represent a more effective way to deposit PTFE coatings on a surface without the additional steps for creating roughness on the deposition surfaces.

Beckford et al. also used this method to ensure adhesion when making PTFE composites [7]. Using PDA coated copper nanoparticles (NPs) as a filler for PTFE, the wear life of the sample doubled compared to PDA/PTFE and is three orders of magnitude longer compared to just PTFE coating. He reports higher toughness, lower delamination and improved adhesion from adding PDA coated NPs.

Some nano- and micro-sized particles, such as black phosphorus, copper, silver, diamond, bronze, carbon and graphite [4, 8-11] are added as fillers to enhance the desirable mechanical properties and improve the wear resistance of PTFE. Goyal reports fillers can reduce the wear rate of PTFE by two to four orders of magnitude [12]. Lee et al. added nanodiamonds to improve the wear resistance of PTFE coatings [11]. He observed a reduction in coefficient of friction (COF) and wear track width both at room temperature and 150 °C when he added up to 4 wt.%

of nanodiamond particles dispersed in PTFE. Beckford, inspired by Lee's promising results, chose a more affordable NP, Cu as his PTFE filler [9]. Copper has good tribological properties like ductility and thermal conductivity. The Cu NPs improved the wear of the samples by a factor of two compared to PDA/PTFE coatings. Beckford also experimented with graphite, gold and silica and obtained better wear life because of adding these particles [13-15]. 3.3% SiO₂/PTFE thin coating composite resulted in improved wear resistance while maintaining a low COF [13].

This study aims to improve wear life of PTFE coating by incorporating NPs to the PDA underlayer of the PDA/PTFE coating that has increased adhesion to substrates as previously shown by Beckford et al. [6]. While other studies mentioned above have added fillers directly to PTFE, we hypothesize that adding NPs to PDA will create roughness that will improve adhesion with the PTFE top layer. Increasing roughness is one of the ways surfaces were prepared for enhancing PTFE adhesion. Thus, roughness and the strong adhesion to PDA should create a strongly adhered PTFE layer which will withstand wear better.

Another hypothesized positive aspect of adding NPs to the underlayer is the increased mechanical strength of the coating. This is because harder NPs than the PTFE polymer will provide increased resilience to the coating when it encounters other surfaces.

The objectives of this investigation are to a) develop a process to incorporate NPs into the PDA underlayer, b) determine the appropriate concentration of NPs for good tribological results, c) thoroughly study the frictional and wear characteristics of samples with NPs in the underlayer.

2. EXPERIMENTAL METHODS

2.1 Sample Preparation

The stainless steel substrates used in this study were type 316 with 0.03” thickness (McMaster CARR 9759K71) cut into 1” × 1” square samples. The samples were cleaned in an ultrasonic bath at 60 °C for 20 minutes by immersion in a 10% Liquinox (Alconox) detergent and reverse osmosis (RO) water solution. The samples were subsequently soaked in acetone, isopropyl alcohol and DI water for 20 minutes each in a 60 °C ultrasonic bath to remove all impurities. After the cleaning process, the samples were blown dry with a nitrogen gas gun.

Three cleaned stainless steel substrates are placed into an acrylic sample holder placed on a rocking shaker heated at 60 °C. 18 mg of Trizma base (Sigma T1503) was dissolved in 0.2 L of DI water to create a tris buffer solution. 30 mg of dopamine hydrochloride (Sigma H8502) was added to this solution to start the polymerization process. This temperature and trizma base provide an alkaline environment for optimum PDA deposition, which occurred on the sample surface for 45 minutes at 25 rpm rocking speed and 7° rocking angle. Colloidal silica dispersion (Nissan Chemicals ST-PS-M) of 20 wt.% concentration was added 5 minutes after the deposition started. The particles are shaped like strings of pearls made of 18-25 nm spherical silica NPs in a length of 80-150 nm based on information from the vendor’s website [16, 17]. 100 µL, 200 µL and 300 µL of the silica solution was used as received to create three sample sets of three substrates each. An additional sample set was made without silica NPs to serve as the control.

Thin coatings of PTFE were deposited by dip coating, a cost effective and simple method. Aqueous PTFE NP dispersion (Dupont TE-3859 DISP 30) containing 60 wt.% was used as received [18, 19]. PTFE dispersion has particles with an average size of 0.22 µm suspended in

water. The samples were coated using a dip coater (KSV Instruments KSV DC) perpendicular to substrate polishing lines at 10 mm/min insertion and withdrawal speeds and a 20 s wait period in between.

After dip coating, the samples were dried at 120 °C on a hot plate for 3 minutes to drive away water. Next, the samples were placed in an oven at 300 °C and 372 °C for 4 minutes each to evaporate the wetting agents and anneal, respectively [18].

2.2 Sample Characterization

A 3D laser scanning confocal microscope (Keyence VK-X260) was used to observe the surfaces before and after each layer of coating was applied and to take qualitative images for surface analysis. Images were taken at 20x, 100x and 150x magnifications. The microscope was connected to a computer for digital image capture and analysis of the PDA/PTFE coatings. The wear tracks on the surface were also imaged using this microscope.

Scanning electron microscopy (SEM, FEI Nova 600 Nanolab) was used to characterize the surface topography and wear of all samples. SEM micrographs were captured at different surface locations to study the microscale topography of the coated surface, the underlayer and the wear tracks.

Water contact angle measurements were performed using a water contact angle goniometer (OCA 15 plus, DataPhysics Instruments GmbH) with 2 μ L DI water droplets on the PDA coating. These measurements were repeated after application of PTFE coating. The water contact angle measurement is used to characterize the wettability of these surfaces.

2.3 Tribological Testing

Tribological testing was performed with a tribometer (Bruker UMT-2) to determine the friction and durability of the coatings. Samples were attached to the stage with double-sided tape. A ball-on-flat configuration was used with chrome steel balls of 6.35 mm diameter. The sliding speed was 10 mm/s, perpendicular to the substrate polish lines and the stroke length was 5 mm. A 5 N force was applied in the normal direction and the test was performed until a sharp increase in COF indicative of the coating wear to the stainless steel substrate. This sharp increase in COF correlates to the failure criterion of 1.5 N frictional force recorded by the friction force sensor. The wear life of the coating is determined by the number of cycles till this sharp increase in COF. The software (UMT CETR) records the position of the ball, the forces in three cardinal directions and the COF for each test.

3. RESULTS AND DISCUSSION

3.1 Surface Topography

Table 1 shows the average roughness values, Ra, and root mean square roughness, Rq and their standard deviation of PDA layer PTFE layer. Figure 1 shows SEM micrographs of the PDA underlayer with varying concentrations of silica added. The control sample with only PDA deposited in figure 1a was rather smooth. Some PDA aggregates are formed and evenly but not densely distributed on the surface. As expected, the addition of silica NPs to this layer increased the roughness of the surface as seen in figures 1b-d. The surface in figure 1b shows PDA with 100 μ L of silica solution. Figure 1b shows a degree of conglomeration of the silica NPs. Figures 1c and d also show aggregation of silica NPs. The difference between the aggregations in these

images is the congregation of particles in figure 1b is more planar while in figures 1c and d, the accumulation is more spherical with a noticeable elevation from the surface. The way the NPs aggregate affects the surface roughness values. Because the particles are spread out with more frequent peaks around the mean line, the 100 μL sample has the highest roughness value, 231 nm. Although the clumps of NPs are bigger overall in figures 1c and d, the roughness values, 207 nm and 200 nm respectively, are smaller. This is because the peaks, although more elevated, are less frequent and more of the surface is without aggregation and thus closer to the mean line. The size of the clumps in the 300 μL sample are wider than those in the 200 μL sample. Thus, as the concentration of silica increases, aggregation of the NPs increases.

SEM micrographs in figure 2 show the needle-like network of PTFE deposited on top of the PDA layer. This network occurs during annealing of the deposited PTFE coating. The overall roughness of the PTFE layer increases with increasing silica concentration. It is clear figures 2a and d show more waviness evident from the high contrast while figures 2b and c show smoother coatings.

The mode of aggregation of silica NPs influences the smoothness and roughness of the top layer. For the control sample without any NPs in figures 2a, roughness of the coating after PTFE application increases from 26 nm to 140 nm. Addition of the PTFE introduces roughness to the previously very smooth PDA sample. A different effect is seen with the samples containing silica NPs. The PTFE fills in the recessed areas not covered by silica.

For the 100 μL silica sample shown in figure 2b, the planar and evenly distributed aggregation across the entire surface of the PDA underlayer (figure 1b) is smoothed by PTFE reducing the roughness from 231 nm to 147 nm. This same effect is noticed in the 200 μL and 300 μL silica samples in figures 2c and d with Ra reduced to 192 nm and 197 nm from 207 nm

and 200 nm respectively. The smoothening effect of PTFE on the PDA surface reduces with increasing silica concentration. The waviness mentioned earlier in figures 2d is due to the high asperities caused by silica aggregation on the PDA surface. Although the silica NPs do not poke through the top layer of the 300 μ L sample, they cause an undulating effect.

For the samples with silica in the underlayer, adhesion of the PTFE is increased because NPs act as barriers to sliding of PTFE. This is evident in figure 3 which shows the interface of PDA and PTFE. For the control sample in figure 3a, there is a transition area from the PDA area to uniform PTFE area where PTFE molecules are unevenly distributed. It is likely the PTFE slipped under gravitational force during the dip coating process because of the smooth PDA coated surface. This adhesion behavior also explains the waviness noticed in the control sample of figure 2a. In the control sample the increased surface area provided by the silica NPs is absent causing slipping and weak adhesion between the PDA surface and PTFE. The presence of NPs in fig 3b-c lead to a more uniform coating without a transition area of low coating thickness. However, too much NPs caused large aggregates as shown in fig 3d, which led to a more wavy PTFE coating than the control sample. Figures 1-3 show the addition of small amount of NPs underneath PTFE leads to increased PDA layer roughness which in turn translates to more even PTFE coatings and improved adhesion to the substrate.

3.2 Surface Wetting Property

Table 2 shows the average water contact angles of PDA layer and PTFE layer. The water contact angle (WCA) for the PDA without any NP added is 64.1° , which is hydrophilic. Silica has a water WCA between $8-18^\circ$ [20]. Therefore, the PDA surfaces became more hydrophilic (decreasing WCAs) with increasing silica concentration. The opposite effect is noticed in PTFE which is hydrophobic. The WCAs increase with increasing silica concentrations in the samples.

A factor affecting the wetting of PTFE surfaces is roughness. According to the Wenzel wetting model, the water contact angle of a hydrophobic surface increases with the surface roughness [21]. With the addition of silica in the underlayer, the surfaces have an increased roughness and thus their hydrophobic nature is enhanced. WCA of the control sample with average roughness of 140 nm is 122° and the WCA of the highest concentration of silica, 300 μ L with average roughness of 197 nm is 130°. The correlation between roughness values and WCAs of PTFE coatings is shown in figure 4.

3.3 Friction and Durability

Results of a preliminary study into the effects of silica in underlayer of PDA/PTFE carried out with 200 μ L, 400 μ L and 600 μ L of silica NP solutions are shown in Figure 5a. It was determined from this pilot study that concentrations above 400 μ L resulted in decreasing wear life of the coatings compared to control. Therefore, the concentrations in the full study were selected to be 100 μ L, 200 μ L and 300 μ L of silica solution in PDA solution. The durability test results shown in Figure 5b are the averages of three tests carried out on each of the three samples in a set of the same silica NP concentration. The average wear life of the control sample is 444 cycles and the addition of silica NPs in PDA affects the durability in different ways. The best performance occurs with 100 μ L of silica NP solution showing a wear life improvement of approximately 70% over the control. Addition of 200 μ L of SiO₂ NPs to PDA underlayer improves the wear life of PTFE coatings by approximately 9%. However, addition of 300 μ L of SiO₂ NPs to PDA underlayer reduces the wear life of PTFE coatings by approximately 60%. The standard deviation of the control sample is high because of the inconsistency of coating thickness from sample to sample leading to a wide variation in wear life. Addition of NPs led to more consistent coatings because the NPs act as anchors for the top layer leading to consistent PTFE

coating thickness. Thus, there is less variation in the durability results of samples with NPs. The wear life in this study is impressive given that a 5 N load was used compared to 50 g load used by Beckford et al. when testing the silica/PTFE composite samples for 1000 cycles each [13].

Figure 6 shows the change in COF of the top performers of PDA/PTFE and PDA + silica/PTFE during durability tests. The spike in the curve is the predecessor of failure of the coatings. During the first 50 s of the test, the COF of all samples rise rapidly as the less dense PTFE particles are plowed away or compacted. The COF curve of the control sample is on an upward trend throughout the test till the coating fails. The 300 μL silica sample has a similar trend from the beginning until around 270 s where there is a slight reduction in COF and then a big jump to failure. The best sample (100 μL silica) has a subtle climb in COF, oscillating between 0.101 and 0.106 from 400 s - 850 s. Between 400 s and 600 s, the COF of the next best performing sample (200 μL silica) has a similar plateau. The two samples with better wear life than the control had smoother PTFE coatings as seen in figures 3b and c while the two samples with worse wear life had more wavy PTFE coatings. Because of the tall asperities in the 300 μL silica sample (figure 1d), the PTFE coating is thinner in some areas like the tops of asperities and thicker in the areas with no aggregation. Consequently, the rubbing surface wears quickly through the thin PTFE on the asperity and meets abrasive silica NPs resulting in increasing COF. A different mode of wear occurs in the control sample. The waviness seen in the control sample's SEM micrograph (figure 3a) is indicative of inconsistency in coating thickness with valley areas of the coating thinner than the average coating thickness. This, coupled with the absence of increased adhesion from the roughness created by NPs in the underlayer, results in the shorter wear life seen in the control sample.

The presence of silica in the coating facilitates the formation of transfer films. In the image of the counter face to the control sample in figure 7a, the ball bearing has very little transfer film which is located close to the abrasion area. Silica in the coating encourages the breakup of PTFE and more transfer films are formed on the counter faces in figures 8b-d. Nanoparticles encourage formation of smaller PTFE debris which attach to the counter face easily and help reduce friction. Transfer films are associated with better wear resistance as the PTFE is reapplied throughout the wear track by the counter face. As the concentration of silica increases, the abrasion on the countersurface becomes wider signifying the hard silica particles are removing material from the counter face as well.

The wear tracks shown in figure 8 are created from the 5 mm stroke length of the ball-on-flat configuration durability test. Common to all wear tracks are buildup on the circumference of the track and a deep groove in the wear path. Representative profiles of these wear tracks are shown in figure 9. The high load applied during the durability test produces rounded wear profiles in the center. All samples have a region of severe wear (groves) in a different location on each sample. The 300 μL silica sample has the deepest wear profile and groove depth. The depth of the groove increases with increasing silica concentration indicating abrasion as a prominent mechanism of wear in this study. Although the 100 μL silica sample had the second deepest overall wear profile, it lasted the longest period with the shallowest groove depth.

Figure 10 shows SEM micrographs of the wear tracks produced on PDA/PTFE control and PDA+SiO₂/PTFE samples. The wear tracks are perpendicular to the direction of polish lines. It can be seen that the region of deepest wear and abrasion does not occur at the exact same location for all samples. The micrographs also show the area of buildup parallel to the wear track where material removed from the track has been deposited.

Inside the wear track area, there are vertical grooves along the sliding direction where material has been ploughed away in the 200 μL silica sample and 300 μL silica sample. The right side of the wear track in 300 μL silica sample has a severe sharp cut. These grooves, indicative of abrasion of the substrate, are associated with poor wear life.

Figure 11a-d show a higher magnification of the deep grooves created in a vertical sliding direction. Pieces of PTFE have been moved about in this region by the counter face. With increasing silica concentration, the samples show smaller PTFE fragments. This is because the NPs encourage fragmentation of PTFE. These smaller pieces of PTFE are easily moved to other locations by the counter face. The 200 μL silica sample has fragments about half the size of those in the 100 μL silica. The fragments present in the 300 μL silica sample (figure 11 d) are even smaller.

The features of the deepest grooves hint at the mechanisms of wear present in these samples. The presence of lines where material seems to be scraped off indicates abrasion. These lines are more frequent with increasing silica concentration. Although silica is absent in the control sample, some abrasion lines are still noticed, but not as sharp as those on the coatings containing silica NPs. These can be attributed to the roughness of the counter face. In figures 11 b-d, the abrasion can be attributed to both the silica particles and the counter face. The SEM micrographs also indicate adhesive wear evident by the presence of debris inside the wear track. The control sample has a relatively “clean” wear track compared to the silica samples. While adhesive wear leads to material being removed, it also contributes to reapplication of PTFE by transfer films and thus longer wear life.

Figures 12a-d show the buildup area beside the wear track. The PTFE in the buildup area has cracks which are longer in the control, figure 12a and become shorter in figures 12b-d. The

presence of silica in the thin coating helps retain PTFE on the surface by causing the top layer to be broken up into smaller pieces which can be reapplied to the wear track by the counter face. When bigger chunks are removed, the coating fails faster. Thus, the fragmentation of PTFE by the ceramic NP helps prolong the wear life. Because silica possesses a high hardness, a balance of breaking up PTFE and avoiding abrasion of both counter face and surface must be found. Therefore, while 300 μL of silica solution provides the best fragmentation of PTFE into smaller particles, it also produces the worst wear life because of the concentration of abrasive silica particles on the surface leads to higher COF and cutting.

4. CONCLUSION

The results indicate adding a small amount of silica NPs to the underlayer of PTFE thin coatings increases the durability of PDA/PTFE coatings. The addition of silica NPs increased the roughness of the PDA layer causing better adhesion of PTFE to PDA. Silica NPs encourage the formation of microcracks on the coating surface which lead to smaller debris size thus slowing material removal from the wear track. Silica also encouraged the formation of transfer film on the countersurface which contributed to the improved wear of the surface. The sample with 100 μL of 20 wt.% silica dispersion performed the best with a 70% increase in wear life over the control. Concentrations of silica higher than 200 μL lead to abrasion of the surface, indicated by the deep wear track and cutting/grooves seen in the SEM micrographs of the 300 μL sample.

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REFERENCES

- [1] Dhanumalayan, E., and Joshi, G. M., 2018, "Performance properties and applications of polytetrafluoroethylene (PTFE) - a review," *Advanced Composites and Hybrid Materials*, **1**(2) pp. 247–268.
- [2] Unal, H., Mimaroglu, A., Kadioglu, U., 2004, "Sliding Friction and Wear Behaviour of Polytetrafluoroethylene and its Composites Under Dry Conditions," *Materials and Design*, **25**(3) pp. 239-245.
- [3] Unal, H., Sen, U., and Mimaroglu, A., 2006, "An Approach to Friction and Wear Properties of Polytetrafluoroethylene Composite," *Materials and Design*, **27**(8) pp. 694-699.
- [4] Harris, K. L., Pitenis, A. A., Sawyer, W. G., 2015, "PTFE Tribology and the Role of Mechanochemistry in the Development of Protective Surface Films," *Macromolecules*, **48**(11) pp. 3739-3745.
- [5] DuPont, T., "Applying Teflon Coatings," http://Rjchase.Com/Application_guidelines.Pdf (Fact Sheet).
- [6] Beckford, S., and Zou, M., 2014, "Wear Resistant PTFE Thin Film Enabled by a Polydopamine Adhesive Layer," *Applied Surface Science*, **292** pp. 350-356.
- [7] Beckford, S., Mathurin, L., Chen, J., 2016, "The Effects of Polydopamine Coated Cu Nanoparticles on the Tribological Properties of Polydopamine/PTFE Coatings," *Tribology International*, **103** pp. 87-94.
- [8] Beckford, S., Cai, J., Chen, J., 2014, "Use of Au Nanoparticle-Filled PTFE Films to Produce Low-Friction and Low-Wear Surface Coatings," *Tribology Letters*, **56**(2) pp. 223-230.
- [9] Beckford, S., Mathurin, L., Chen, J., 2015, "The Influence of Cu Nanoparticles on the Tribological Properties of Polydopamine/PTFE + Cu Films," *Tribology Letters*, **59**:11.

- [10] Peng, S., Guo, Y., Xie, G., 2018, "Tribological Behavior of Polytetrafluoroethylene Coating Reinforced with Black Phosphorus Nanoparticles," Applied Surface Science, **441** pp. 670-677.
- [11] Lee, J., and Lim, D., 2004, "Tribological Behavior of PTFE Film with Nanodiamond," Surface and Coatings Technology, **188-189**(1-3) pp. 534-538.
- [12] Goyal, R. K., and Yadav, M., 2014, "The Wear and Friction Behavior of Novel Polytetrafluoroethylene/Expanded Graphite Nanocomposites for Tribology Application," Journal of Tribology, **136**(2) pp. 021601.
- [13] Beckford, S., Wang, Y. A., and Zou, M., 2011, "Wear-Resistant PTFE/SiO₂nanoparticle Composite Films," Tribology Transactions, **54**(6) pp. 849-858.
- [14] Beckford, S., Osborn, L., Zou, M., 2011, "Tribological study of PTFE/Au nanoparticle composite thin films," ASME/STLE 2011 International Joint Tribology Conference, IJTC 2011, October 24, 2011 - October 26, Anonymous American Society of Mechanical Engineers (ASME), Los Angeles, CA, United states, pp. 1-3.
- [15] Beckford, S., Cai, J., Fleming, R. A., 2016, "The Effects of Graphite Filler on the Tribological Properties of Polydopamine/PTFE Coatings," Tribology Letters, **64**:42.
- [16] Nissan, C., "SNOWTEX," <https://Nissanchem-Usa.Com/Products/Snowtex/>.
- [17] Semiconductor, O., "SNOWTEX Typical Properties," <https://Www.Semiconductoronline.Com/Doc/Snowtex-Typical-Properties-0001>.
- [18] DuPont, T., 2015, "Teflon PTFE DISP 30," https://Www.Fuelcellearth.Com/Wp-Content/Uploads/Converted_files/Pdf/DISP_30.Pdf .

[19] DuPont, T., 2017, "Dispersion Properties and Processing Guide," https://www.fuelcellearth.com/wp-content/uploads/converted_files/pdf/disp30-msds.pdf .

[20] Fleming, R. A., and Zou, M., 2013, "Silica Nanoparticle-Based Films on Titanium Substrates with Long-Term Superhydrophilic and Superhydrophobic Stability," *Applied Surface Science*, **280** pp. 820-827.

[21] Sigmund, W.M., and Hsu, S., 2016, "Encyclopedia of Membranes," Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 310-311.

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Table 1: Average roughness values, Ra, and root mean square roughness, Rq, and their standard deviation of PDA layer PTFE layer

Sample	Ra (nm)	Ra SD (nm)	Rq (nm)	Rq SD (nm)
Control, PDA only	26	1.6	36	1.7
PDA + 100 μ L silica	231	25.3	338	32.5
PDA + 200 μ L silica	207	24.5	342	36.8
PDA + 300 μ L silica	200	25.0	311	27.0
Control, PDA/PTFE	140	2.3	167	3.5
PDA + 100 μ L silica /PTFE	147	1.9	178	1.6
PDA + 200 μ L silica/PTFE	192	3.3	228	3.7
PDA + 300 μ L silica/PTFE	197	15.4	240	22.0

Table 2: Average water contact angle of PDA layer and PTFE layer

Sample	Water contact angle (°)	SD
Control, PDA only	64.1	0.72
PDA + 100 μ L silica	48.4	0.15
PDA + 200 μ L silica	30.6	2.29
PDA + 300 μ L silica	32.5	1.27
Control, PDA/PTFE	122.6	1.50
PDA + 100 μ L silica /PTFE	123.5	1.37
PDA + 200 μ L silica/PTFE	123.1	1.24
PDA + 300 μ L silica/PTFE	130.5	0.86

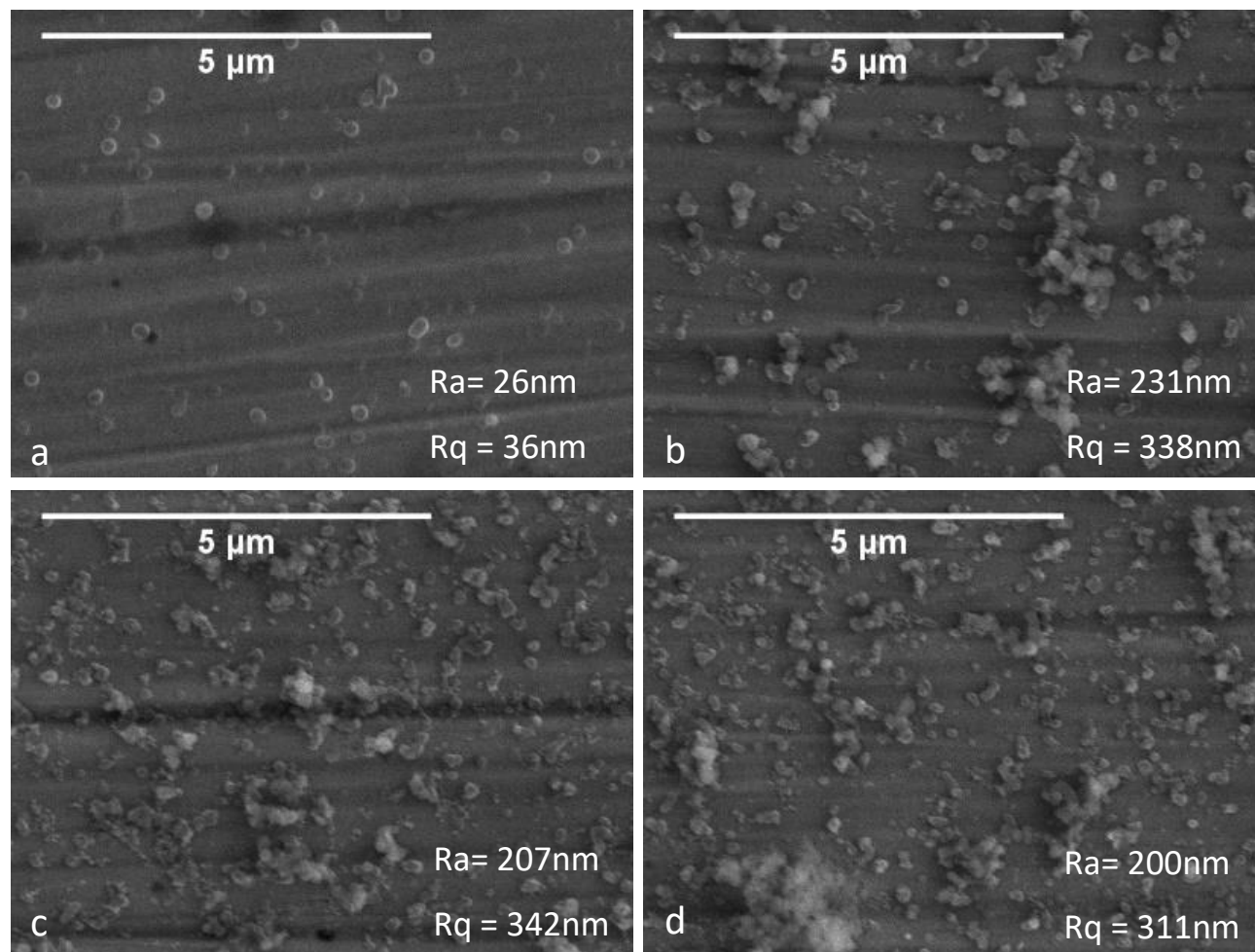


Figure 1: SEM micrographs of steel substrates with (a) PDA (control), (b) PDA + 100 μL silica, (c) PDA + 200 μL silica, and (d) PDA + 300 μL silica

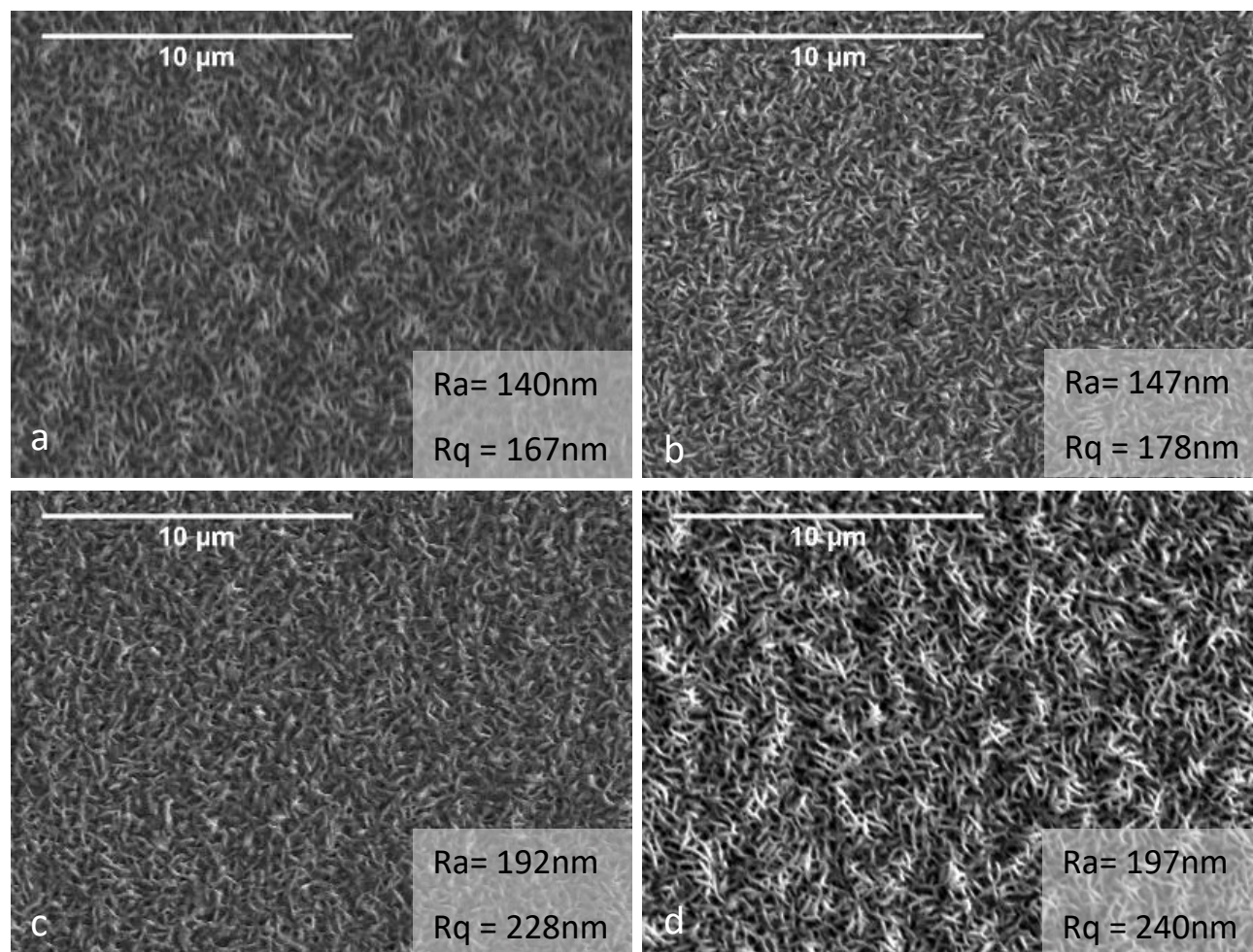


Figure 2: SEM micrographs of steel substrates annealed with (a) PDA/PTFE (control), (b) PDA + 100 μL silica/PTFE, (c) PDA + 200 μL silica/PTFE, and (d) PDA + 300 μL silica/PTFE

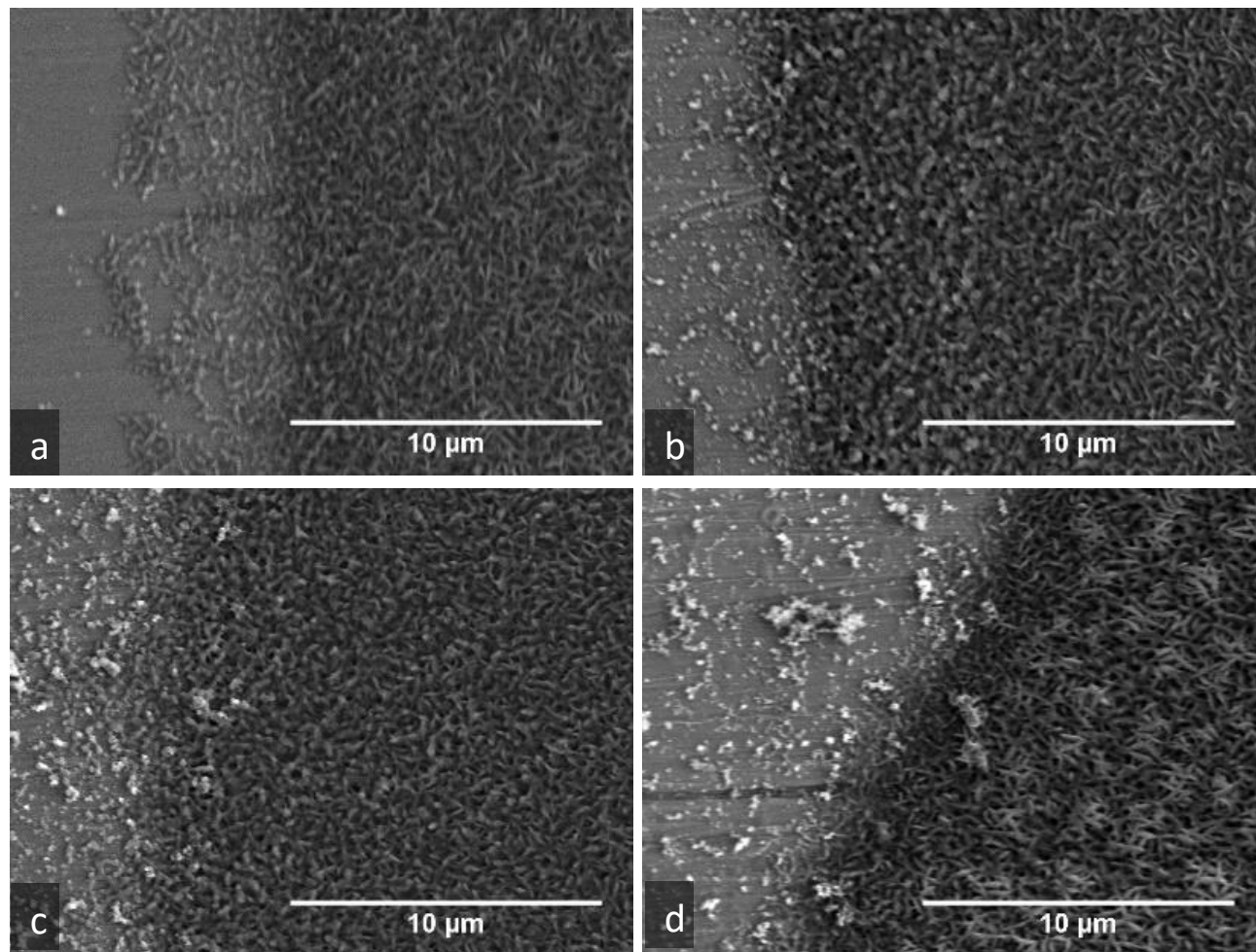


Figure 3: SEM micrographs of steel substrates interface of (a) PDA/PTFE (control), (b) PDA + 100 μL silica/PTFE, (c) PDA + 200 μL silica/PTFE, and (d) PDA + 300 μL silica/PTFE

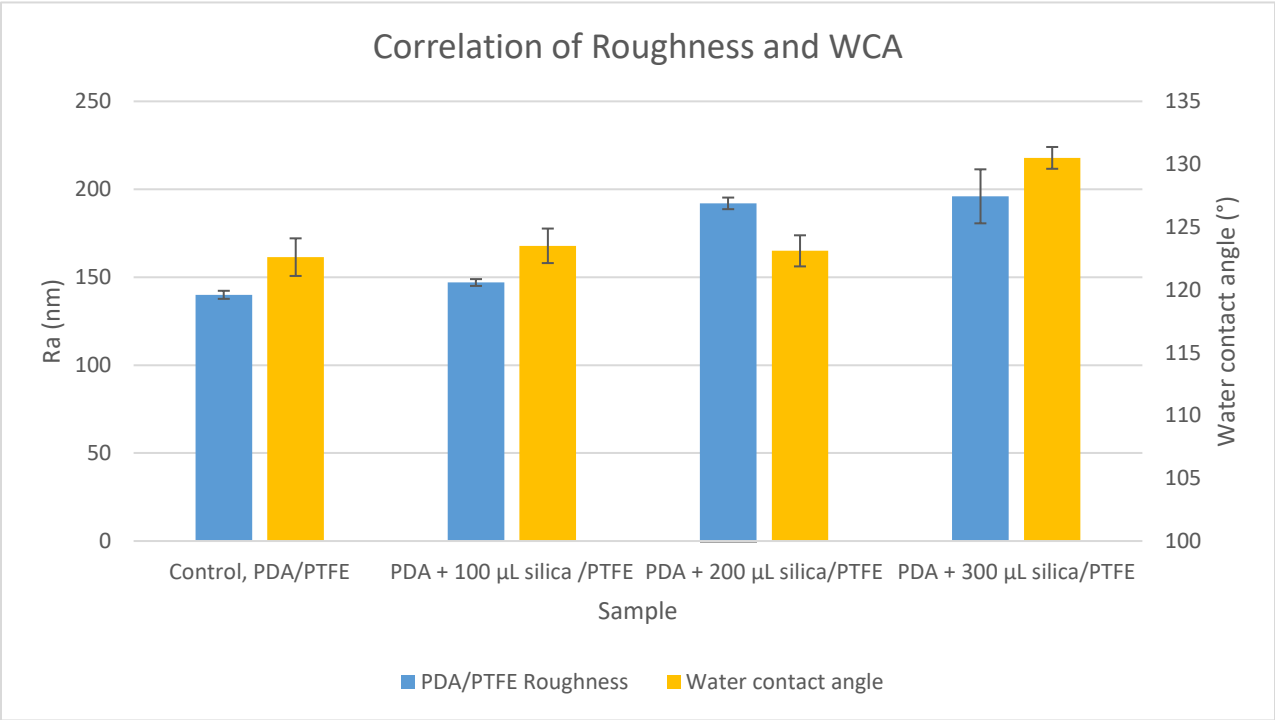


Figure 4: Roughness and water contact angle correlation chart

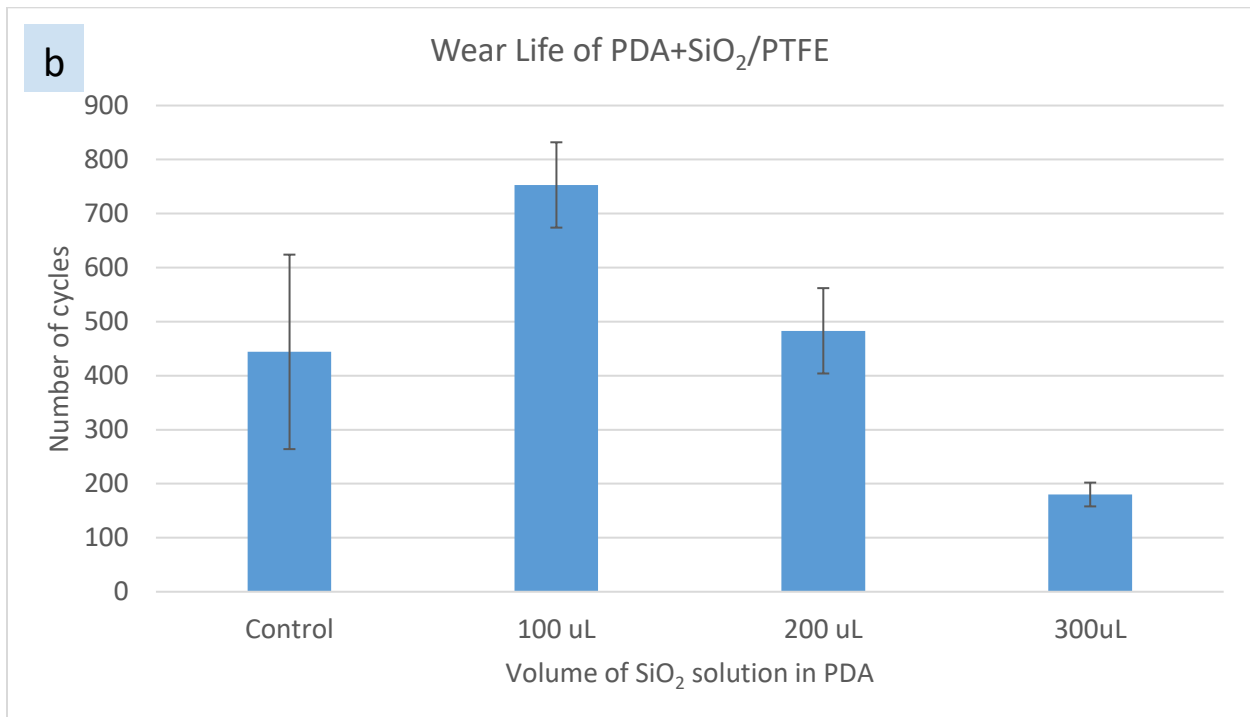
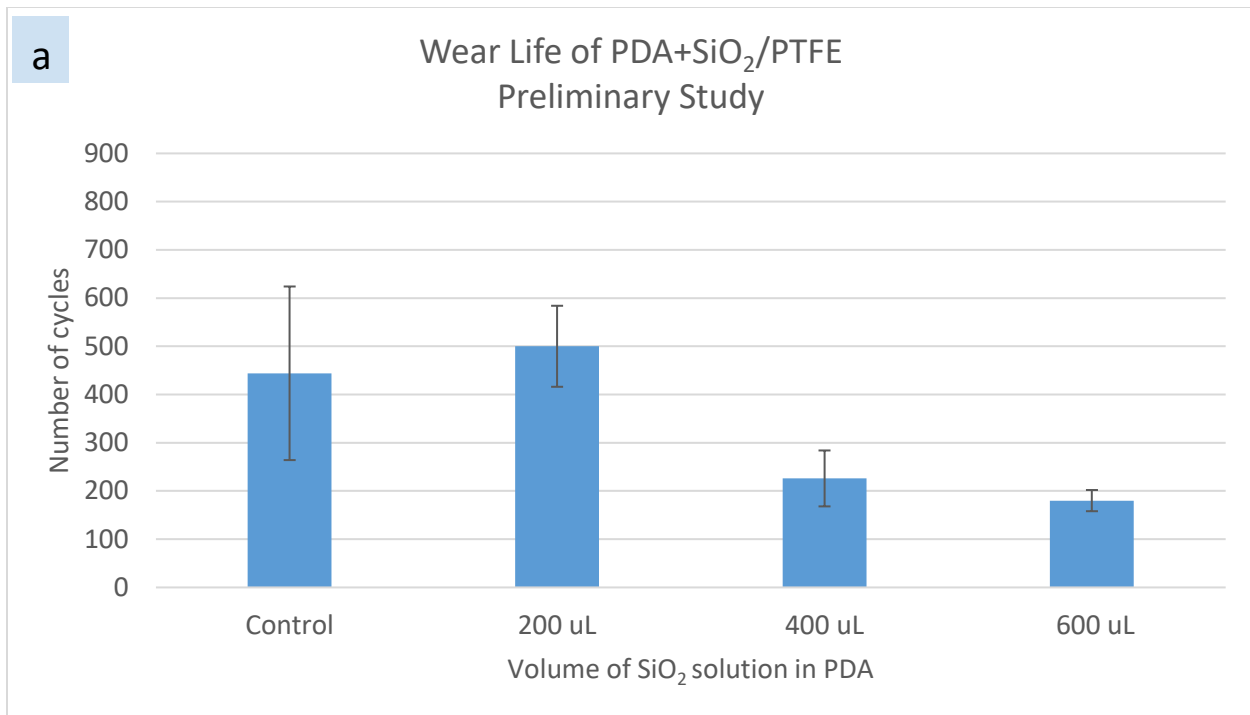


Figure 5: (a) Preliminary study showing average cycles before failure for 5N durability test on control, PDA + 200 μ L silica/PTFE, PDA + 400 μ L silica/PTFE and PDA + 600 μ L silica/PTFE (b) Average cycles before failure for 5N durability test on control, PDA + 100 μ L silica/PTFE, PDA + 200 μ L silica/PTFE and PDA + 300 μ L silica/PTFE

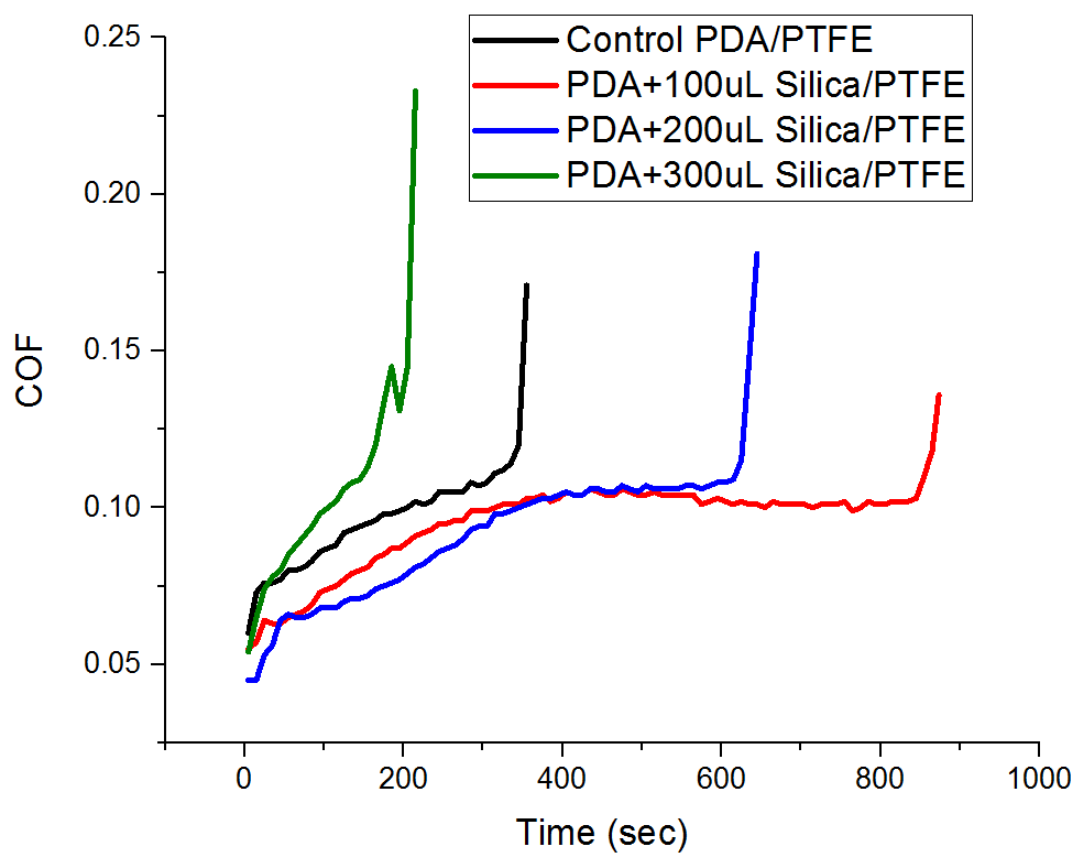


Figure 6: Plot of coefficient of friction as a function of rubbing cycles for PDA/PTFE, PDA + 100 μ L silica/PTFE, PDA + 200 μ L silica/PTFE, and PDA + 300 μ L silica/PTFE

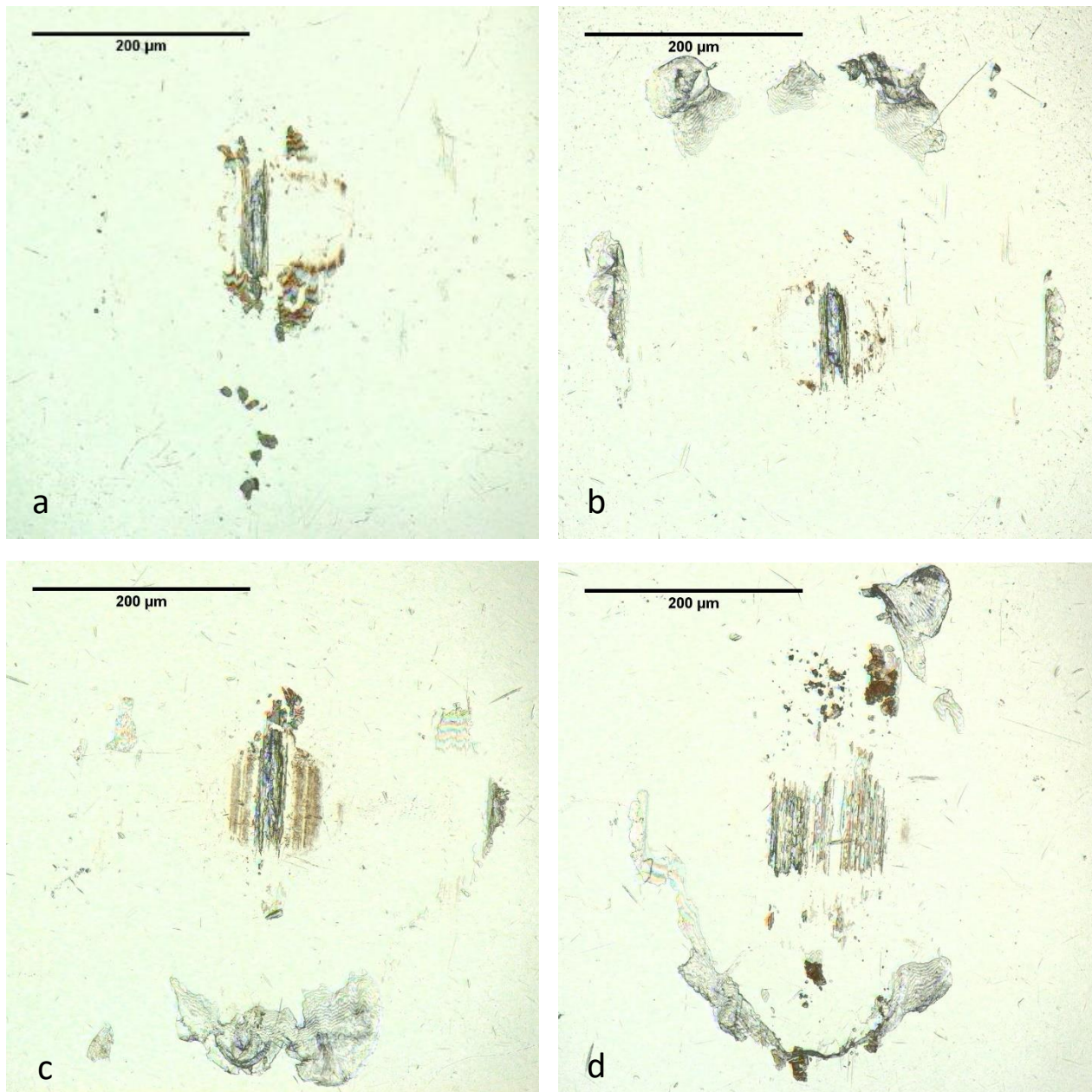


Figure 7: Optical images of counter face for wear tracks on (a) PDA/PTFE (control,) (b) PDA + 100 μ L silica/PTFE, (c) PDA + 200 μ L silica/PTFE, and (d) PDA + 300 μ L silica/PTFE

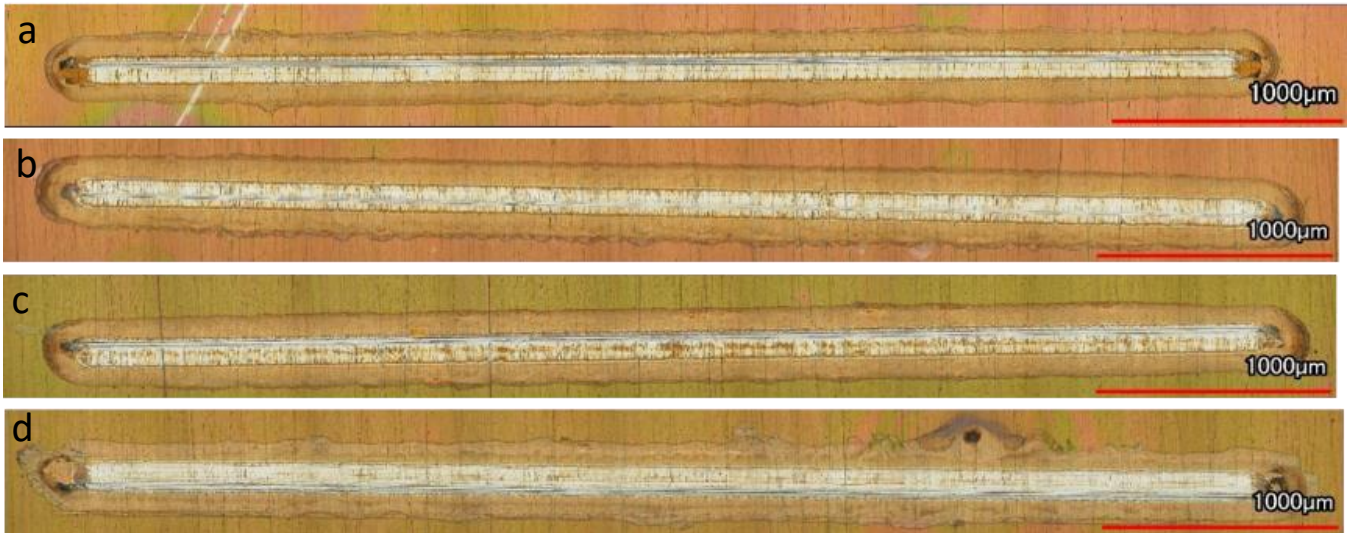


Figure 8: Optical images of wear track of (a) PDA/PTFE control wear track, (b) PDA + 100 μL silica/PTFE wear track, (c) PDA + 200 μL silica/PTFE wear track, and (d) PDA + 300 μL silica/PTFE wear track

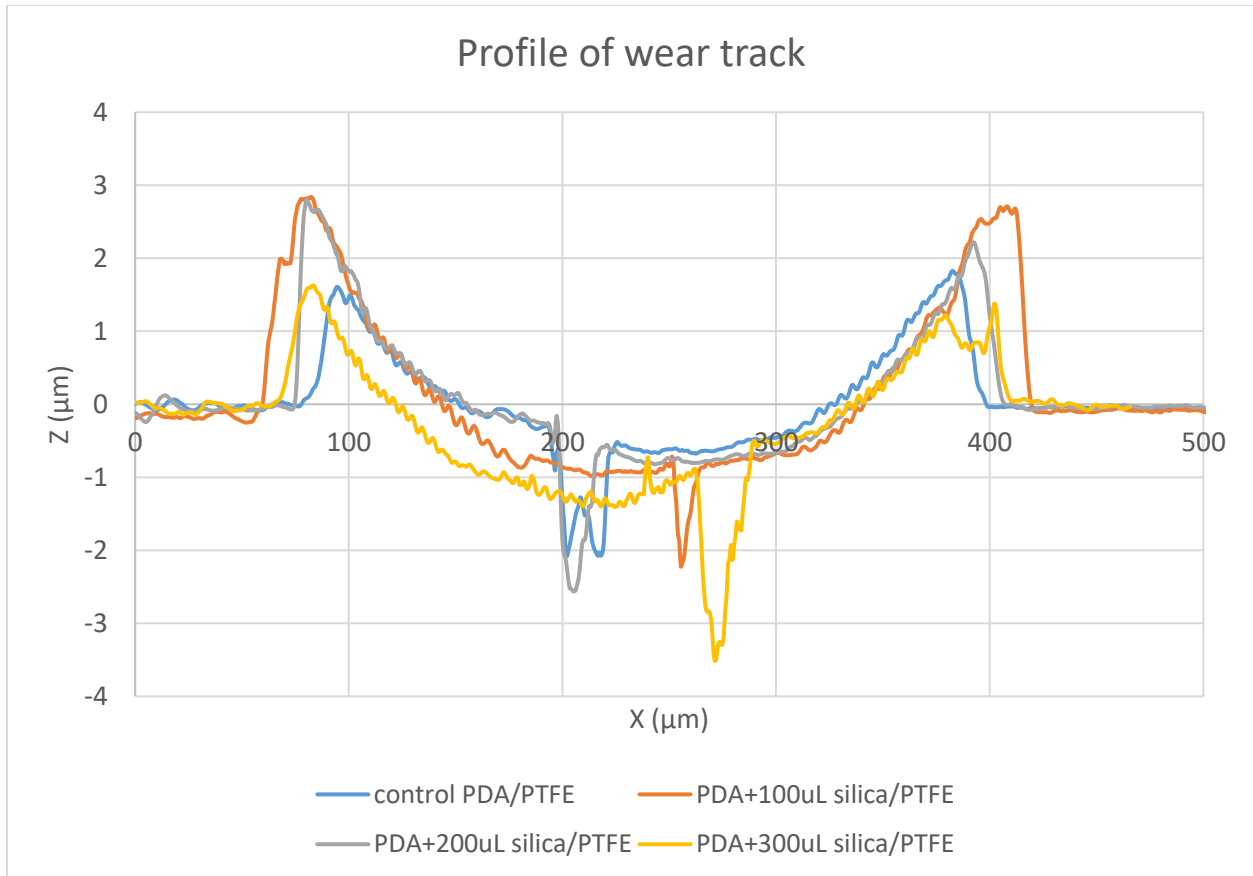


Figure 9: Wear depth profiles of (a) PDA/PTFE control wear track, (b) PDA + 100 μL silica/PTFE wear track, (c) PDA + 200 μL silica/PTFE wear track, and (d) PDA + 300 μL silica/PTFE wear track

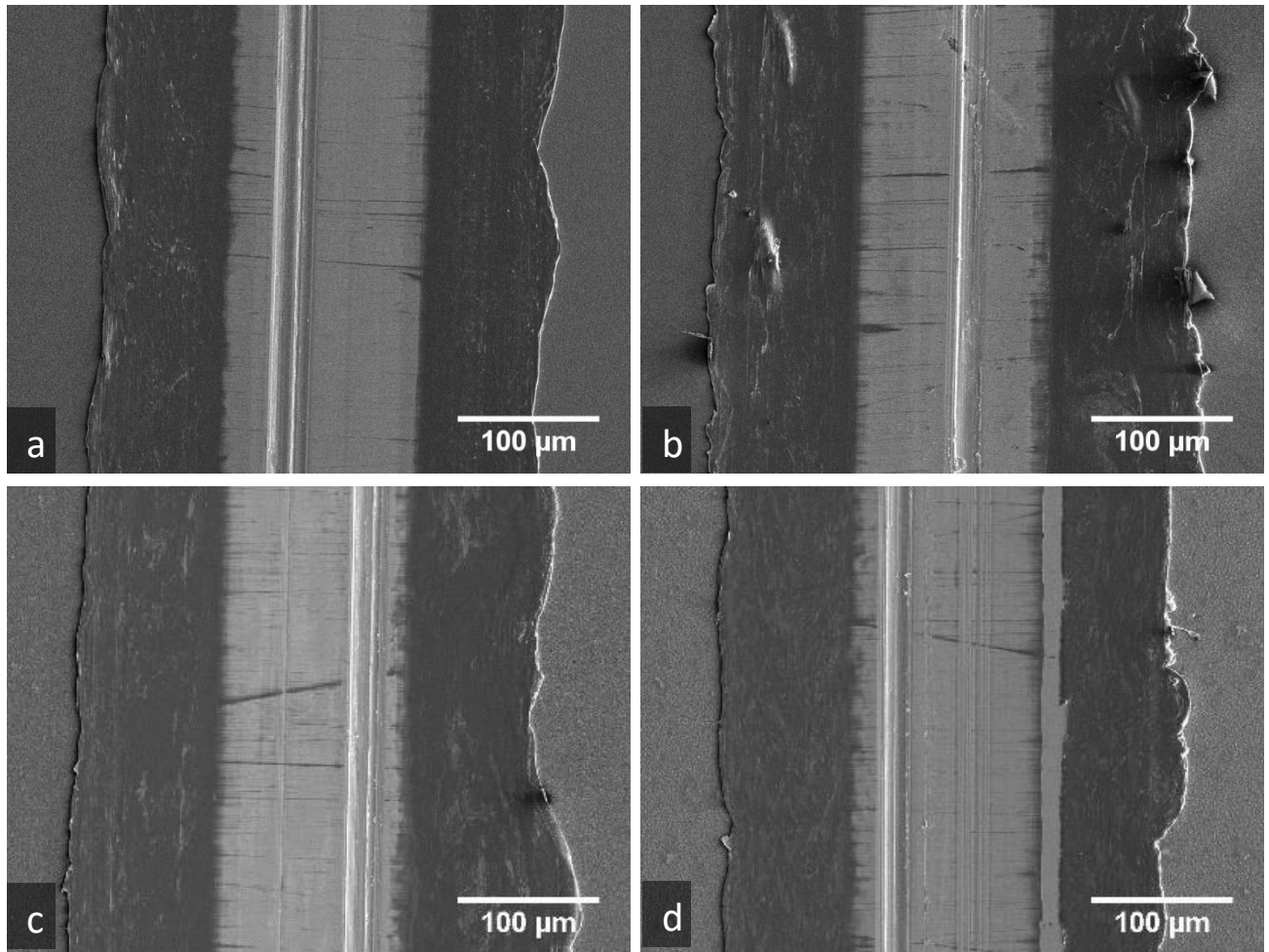


Figure 10: SEM micrographs of wear tracks on a) PDA/PTFE (control), (b) PDA + 100 μL silica/PTFE, (c) PDA + 200 μL silica/PTFE, and (d) PDA + 300 μL silica/PTFE

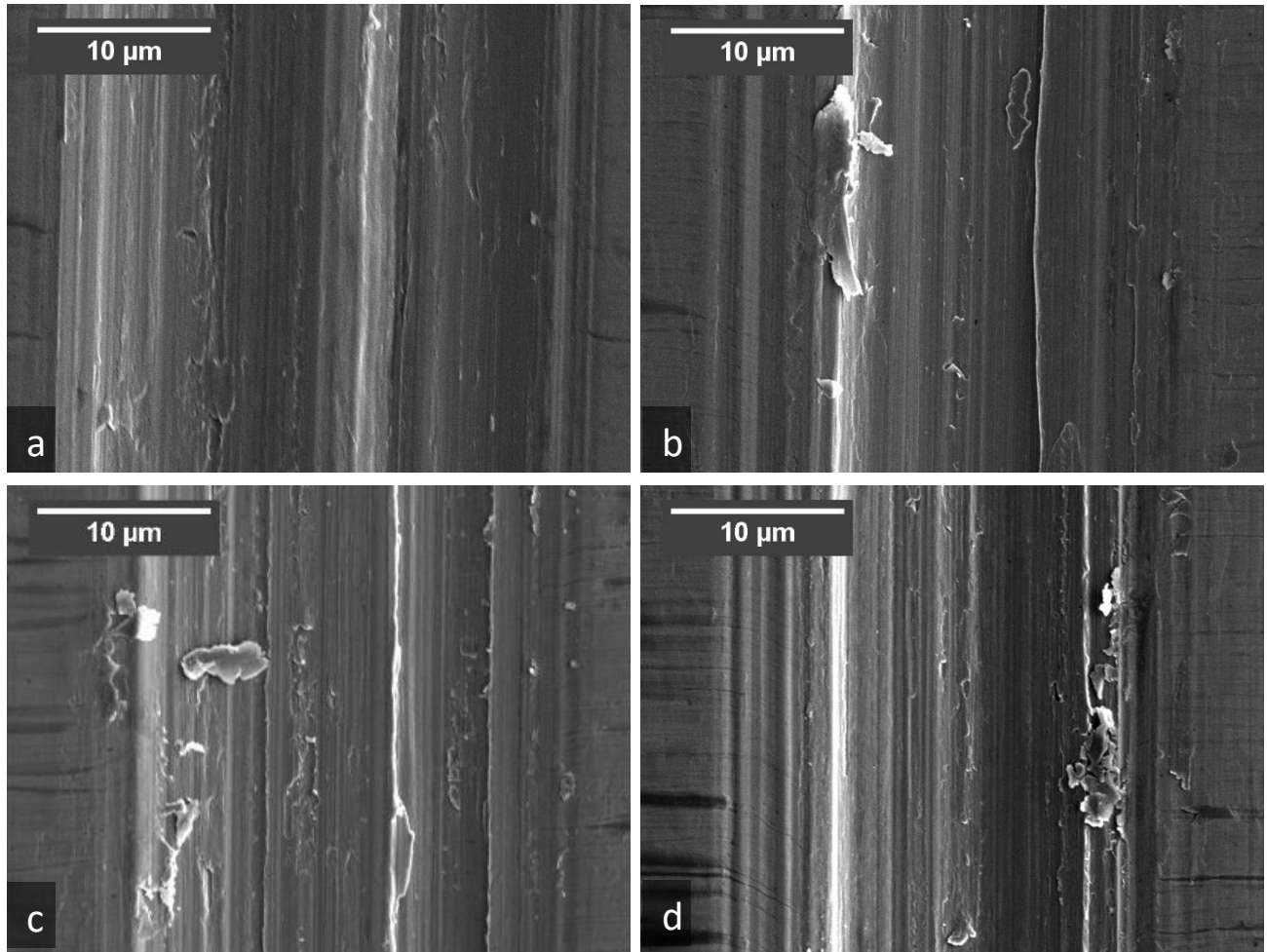


Figure 11: SEM micrographs of wear track inner crack on (a) PDA/PTFE (control), (b) PDA + 100 μL silica/PTFE, (c) PDA + 200 μL silica/PTFE, and (d) PDA + 300 μL silica/PTFE

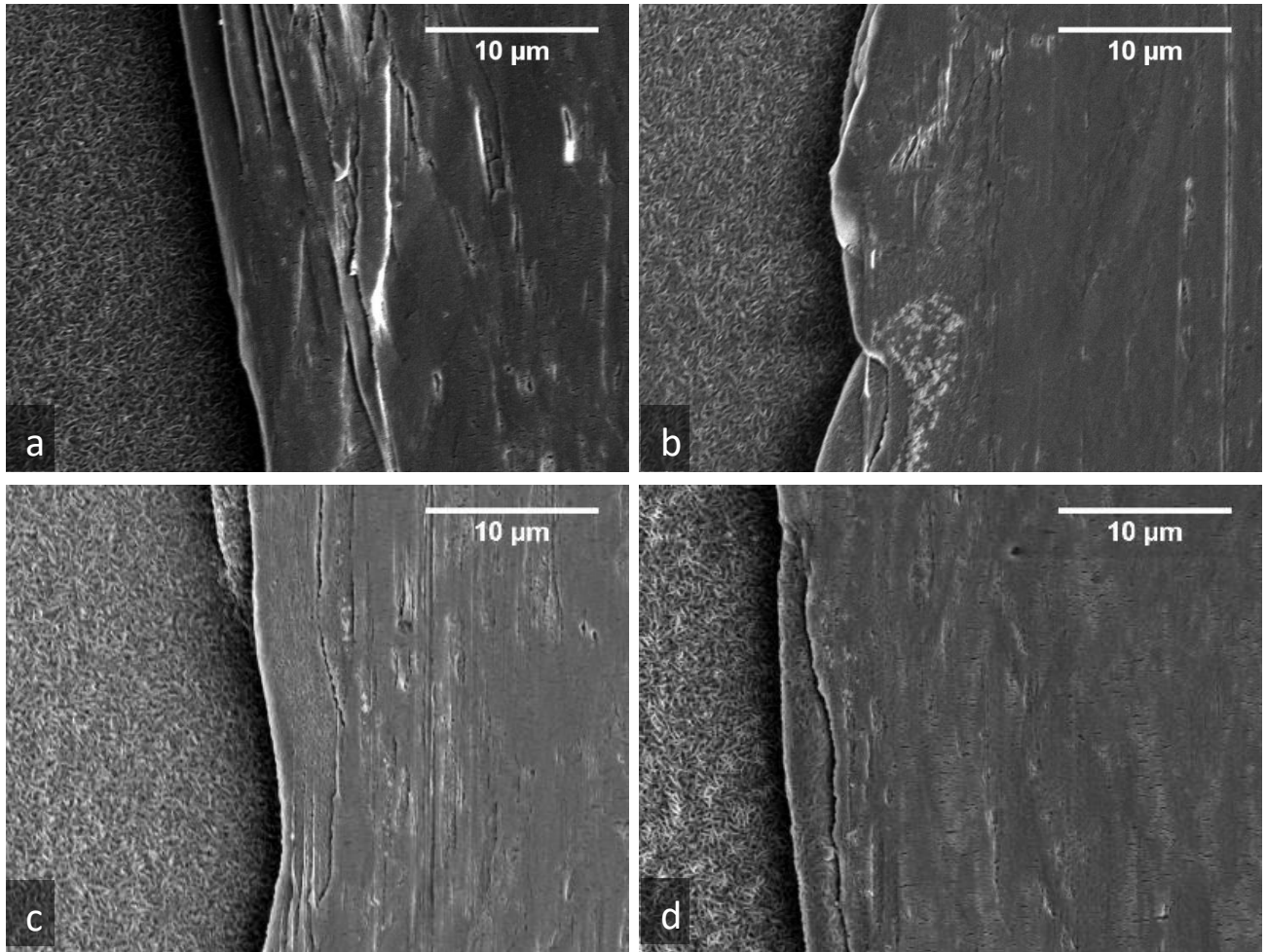


Figure 12: SEM micrographs of wear track buildup on (a) PDA/PTFE (control), (b) PDA + 100 μL silica/PTFE, (c) PDA + 200 μL silica/PTFE, and (d) PDA + 300 μL silica/PTFE