

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to the Department of Defense, Executive Service Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE (DD-MM-YYYY) 05-11-2012		2. REPORT TYPE FINAL		3. DATES COVERED (From - To) 23 Sep 2011 – 23 Sep 2012	
4. TITLE AND SUBTITLE Polymer/Carbon Nanotube Networks for Smart, Self-Repairing and Light-Weighted Nanocomposites			5a. CONTRACT NUMBER W911NF-11-1-0286		
			5b. GRANT NUMBER R&D 1478-MS-01		
			5c. PROGRAM ELEMENT NUMBER		
5. AUTHOR(S) Dr. J. Zekonyte			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
6. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Univeristy of Southampton University Road Southampton, SO17 1BJ UK				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) USAITC-A Building 188 86 Blenheim Crescent, Ruislip, Middlesex, HA4 7HL UK				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for Public Release, distribution is unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The aim of the project was develop smart, strong, and light-weight polymer/carbon nanotube (CNT) composites which will sense tribologically induced damages and self-heal by inhibiting such degradation mechanisms, so preventing failure of the composite. The main focus was on the preparation of new multifunctional coatings and thin films. By incorporation of CNTs we expected to create films with increased surface hardness and resistance to failure. We intended to prepare composites with conducting CNTs acting as composite matrix enhancer, as well as self-healing promoter. The self-healing should be induced by passing an electric current through the network of conducting CNTs. It was expected that polymer matrix in contact with CNT would have been locally heated resulting in increased polymer chain mobility and reorientation, thus sealing the crack, while still avoiding polymer thermal degradation.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 36	19a. NAME OF RESPONSIBLE PERSON
a.REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code)

Final Report for the whole period of 23 September, 2011 – 22 September, 2012

Statement of the problem studied

The aim of the project was develop smart, strong, and light-weight polymer/carbon nanotube (CNT) composites which will sense tribologically induced damages and self-heal by inhibiting such degradation mechanisms, so preventing failure of the composite. The main focus was on the preparation of new multifunctional coatings and thin films. By incorporation of CNTs we expected to create films with increased surface hardness and resistance to failure. We intended to prepare composites with conducting CNTs acting as composite matrix enhancer, as well as self-healing promoter. The self-healing should be induced by passing an electric current through the network of conducting CNTs. It was expected that polymer matrix in contact with CNT would have been locally heated resulting in increased polymer chain mobility and reorientation, thus sealing the crack, while still avoiding polymer thermal degradation.

Technical Overview of the whole period of performance

Within the 12 month of project, few separate and at the same time relating aspects had to be covered. One of the most important problems was to obtain uniformly dispersed nanotubes in solvents as well as polymer matrix. To prepare stock solution, various commercially obtained CNT were dispersed in Toluene : Choloform mixture using high power sonication probe. However, CNT dispersion in polymer matrix was not uniform, and a region of high and low CNT concentration was noted. Recently, an improved CNT dispersion in solutions using various steps of filtering, sonication and stirring was obtained, resulting in better nanotube distribution within polymer matrix.

Mechanical properties of pure polystyrene and polystyrene/CNT composites were measured to characterize composite hardness and modulus. Slight improvement in mechanical properties was observed on polymer composites. As these experiments were done within the first half of the project, little difference in measured properties was attributed to poor nanotube dispersion within the polymer matrix.

The first polymer “healing” attempt was done by heating scratched samples around glass transition temperatures, T_g . “Full healing” was observed after heating samples at temperatures above T_g , and “partial healing” was noted at T_g . Prolonged heat treatment showed composite resistance to thermal degradation.

Finally, conducting nanocomposites were prepared, and their electrical properties were measured using advanced AFM modes. Electrical properties greatly depended on CNT concentration in polymer matrix. By applying a voltage bias between the substrate and conducting cantilever that is constantly in contact with the sample, a current flow is generated. We expected, that generated current flow will be enough to heat the sample locally to trigger polymer chain mobility and reorientation to promote “self-healing”. The concept of polymer composite self-healing by passing current through the sample was proved by measuring composite’s topography, friction and current maps for a period of time.

Summary of the most important results, achievements and outlook

1. The most important results were obtained within the last three month, which are reported in detail in the 4th interim report given below:
 - 1.1. Improved CNT dispersion within solvents. After few cycles filtering, sonication and stirring, nanotubes started to disentangle, and individual CNTs were imaged. The dispersion remained stable for up to 2 – 3 month in polar solvents like toluene and chloroform. Improved dispersions resulted in preparation of uniform nanocomposites.
 - 1.2. Preparation of conducting composites with various CNT concentrations. Electrical properties greatly depended on CNT concentration in polymer matrix. The concept of polymer composite self-healing by passing current through the sample was proved by measuring composite’s topography, friction and current maps for a period of time, and recording the change in scratch artificially made with AFM tip.
2. The latest work generated interesting results (some of which cannot be explained at present), and new ideas for at least 2-3 new projects.
3. The research paper is in preparation and should be submitted to scientific journal as soon as it will be finished.
4. Thanks to the present grant, we were able to purchase important instruments (high power sonicator, current sensing AFM nose cone with pA resolution), AFM software upgrade, and various consumables.
5. Small amount of money were used for small conference fees: UK-China School, Southampton, April 2012; Post Graduate Conference, Southampton, November 2012. No results were presented at those conferences, as the most interesting of them were obtained just recently.
6. The project was carried out by myself, Dr. J. Zekonyte, with consultancy input from Dr. I. Nandhakumar. No other scientific personnel were employed.
7. This grant was included as one of support references for EPSRC instrument grant application for Micro Materials NanoTest Vantage Testing Suite with NTX4Controller. The grant EP/K005103/1 was rewarded in June 2012. The new nanoindenter/nanoscratcher instrument will help greatly to obtain missing results.

4th Interim Report for the period of 23 June – 22 September, 2012

Abstract (this report)

The report summarizes the progress that was made in the last 3 months of the project. We have improved carbon nanotube dispersion in solutions using various steps of filtering, sonication and stirring. Composite electrical properties measured using advances AFM modes, showed dependence on CNT concentration in polymer. The concept of polymer composite self-healing by applying current to the sample surface was proved.

1. Experiments

2.1 Materials

High molecular weight polystyrene (PS) was chosen as a polymer matrix for polymer/carbon nanotube composites. Details of PS and various multiwall carbon nanotubes (MWCNT) were given in previous reports.

2.2 Sample Preparation

2.2.1 Improved CNT dispersion in solvents

CNTs were dispersed in the solvent mixture of toluene and chloroform with ratio 1:1, as reported previously. It was noted that 2 month after solution preparation some precipitants were observed at the bottom of the vial. The rest of the solvent had dark yellow color indicating that reasonable amount of CNTs remained dispersed. The dark yellow solvent was filtered into a new vial using PTFE 0.2 μm filter. Filtered CNT solution was further subjected to sonication using high power ultrasonic horn for 20 - 30 min. Then 10 μl solution was deposited onto the mica, left to evaporate overnight, and later imaged with AFM (Figure 1).

Precipitants were further diluted with toluene : chloroform = 1:1, sonicated for 20 – 30 min, then stirred using magnetic stirrer for 2-5 hours to separate excess of CNT in the solution in the form of precipitants. Every time the remaining dark yellow solvent was filtered and then further sonicated to improve CNT dispersion.

2.2.2 PS/CNT composites

PS/CNT composites were prepared as reported previously. This time filtered-sonicated CNT solution was used. CNT content in PS matrix was 10, 30, 50, and 80 % vol. 4 ml of PS/CNT solution was poured

into 2.5 x 2.5 cm aluminium moulds, and left to evaporate overnight in air in the fume-cupboard at RT. The composites were then heat treated to allow residual solvent evaporation and chain relaxation. Samples were placed in oven and slowly heated (2 °C/min) to 100°C, hold at the temperature for 60 min, then again slowly increased to 110°C for another hour, then cooled to RT at the same rate of 2 °C/min. This time cross-sections of composites were investigated as well. Cut films of 20 mm length, were placed into 7 mm diameter plastic tubes. Melted wax was poured into the tubes, and left to solidify overnight. Prepared “cylinders” were cut into 5 - 6 mm height discs. Samples were shaved using microtome to get smooth, horizontal surfaces.

2.3 Sample Analysis

Surface analysis was done using optical profilometer InifineFocus (Alicona) and atomic force microscope using current sensing, tapping, and Kelvin force (or surface potential) modes.

3. Results and Discussion

3.1 Improved CNT dispersion

One of the greatest problems we have faced in the project, was CNT dispersion in solvents as well as polymer matrix. With multiple filtering, sonicating and stirring procedures, as described above, we have succeeded at some degree to disperse CNTs into solvents at some degree. As shown in Figure 1, after the 1st solution filtering nanotube agglomerates become flatter, than previously reported. The forest of entangled, individual nanotubes could be observed. All consequent CNT solution preparations gave the same result.

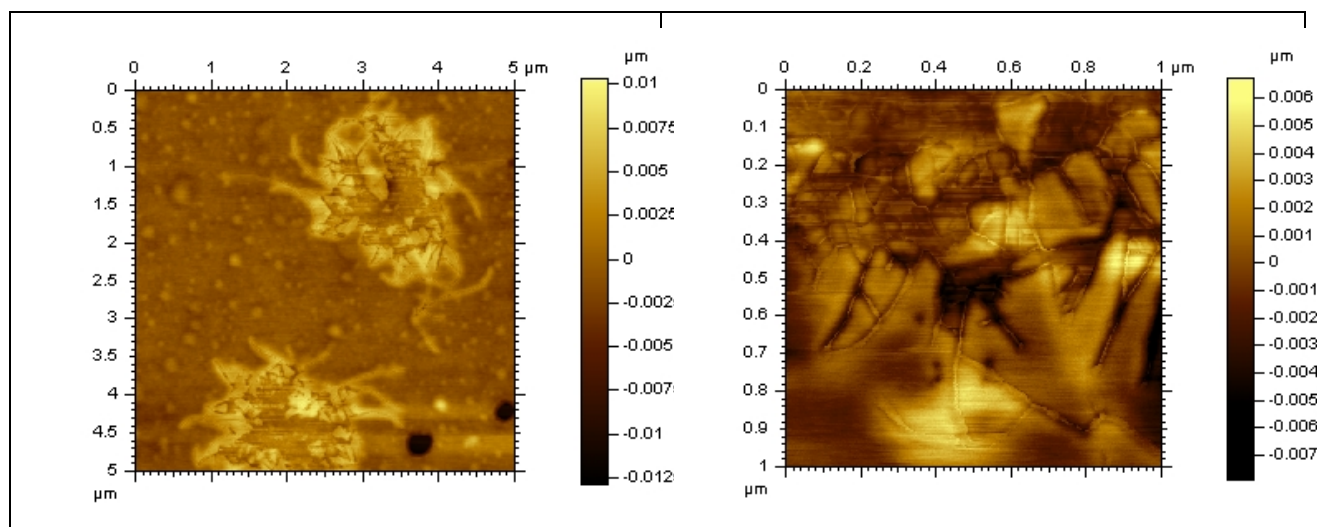


Figure 1. Graphitized CNTs after solution was 1st time filtered and then sonicated.

As stated in previous reports, when polymer composites from concentrated polymer solution were prepared, it was noted that the top side (in contact with air) was more transparent while the back side (in contact with the mould) looked mat. It seemed that while solvent was evaporating, CNTs were pushed down towards the bottom of the composite. The cross section images of composite showed a clear region of high and low CNT concentration (Figure 2 (a), PS solution concentration 180g/l, CNT content 10 vol%). This might have been the reason, why we did not observe large difference in mechanical and tribological properties between virgin PS and PS/CNT composite, as reported in 2nd interim.

When filtered nanotube solutions were used for composite preparation, much better CNT dispersion in the polymer matrix was observed (Figure 2 (b) and (c)). Composite preparation protocol was the same. The only difference was CNT solution preparation. However, it was enough to achieve much better CNT distribution, as no high and low CNT concentration regions were observed under optical microscope.

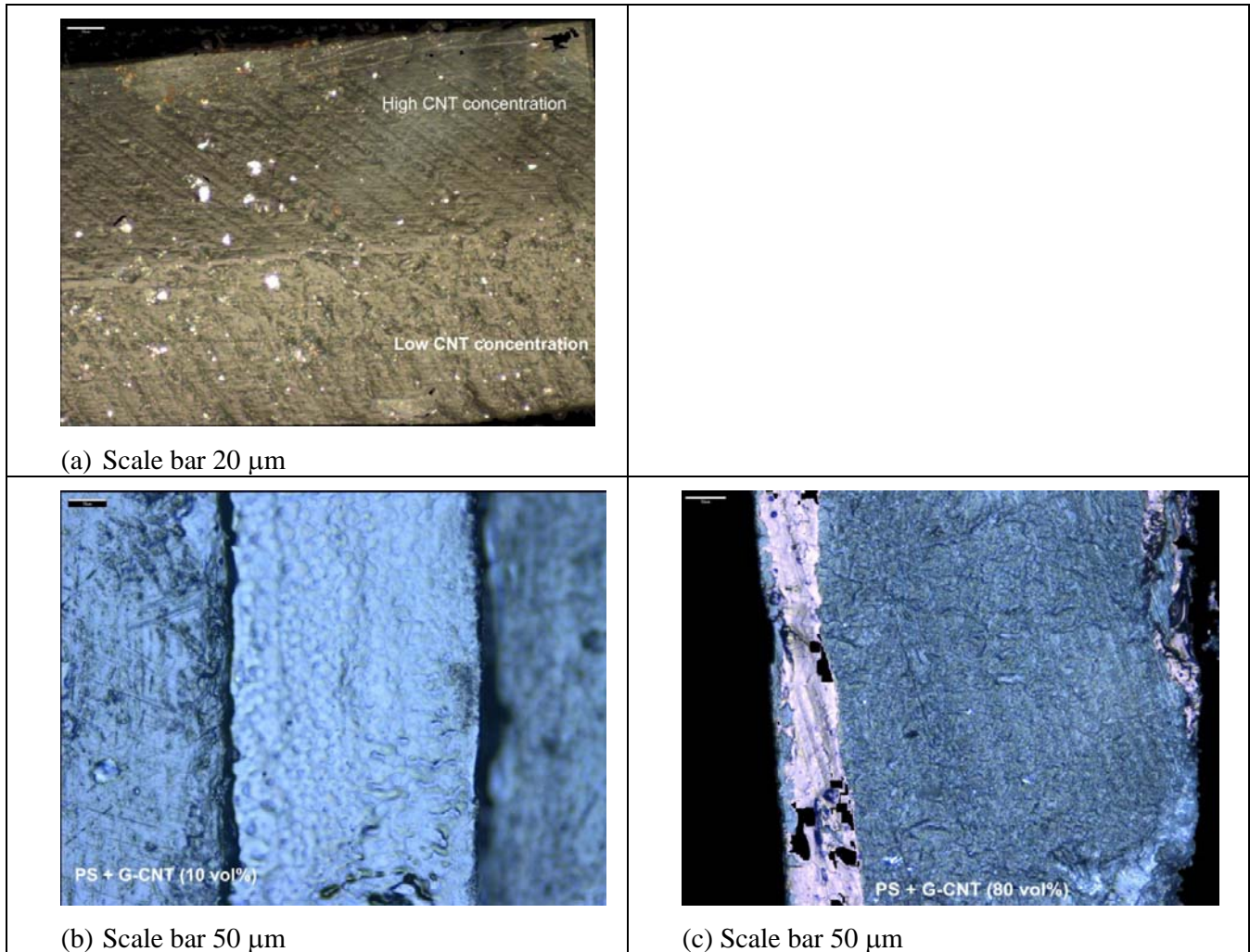


Figure 2. Optical images of polymer/nanotube composite cross-section. Composites prepared from PS solution concentration of 180 g/l with G-CNT concentrations (a) 10 vol% as reported in 3rd interim; (b) 10 vol% and (c) 80 vol% with improved CNT dispersion.

3.2 PS/CNT composites

3.2.1 Mechanical properties

Unfortunately, we were unable to investigate mechanical and tribological properties of composites this quarter using well established standard techniques. This was mainly due to the unfortunate complete failure of nanoindenter/nanoscratcher instrument. Instead, we used atomic force microscope to compare some properties of the composites at some extent. To use AFM as nanoindenter/nanoscratcher isn't straight forward, and a lot of calibration is needed. However, comparative studies are available if the same parameters are used.

Using force spectroscopy mode, film surfaces were indented with AFM tips at loads of 600 nN. Then the final depth of the indent imprint was measured. Figure 3, compares composites with CNT concentration of 10 and 80 vol%, as an example. Comparing those two samples it seems that composite containing 10vol% CNT is slightly harder, as the remaining indentation depth is around 3-3.5 nm comparing to 5nm for CNT 80 vol%. However, this well might be within error range. Furthermore, as AFM tip is much smaller than conventional indenter tip, it would be easier to hit various regions on the surface that will be pure polymer matrix, as well as nanotube. Therefore, hundreds of indents are needed to have good statistics, and force maps of the surfaces would be important to identify composite properties. This special mode usually takes the whole day to measure one region of one sample generating thousands of force-displacement curves and force maps. Our AFM software just recently has been upgraded (courtesy of the present grant) to be able to perform such measurements, and most important to run macro data analysis.

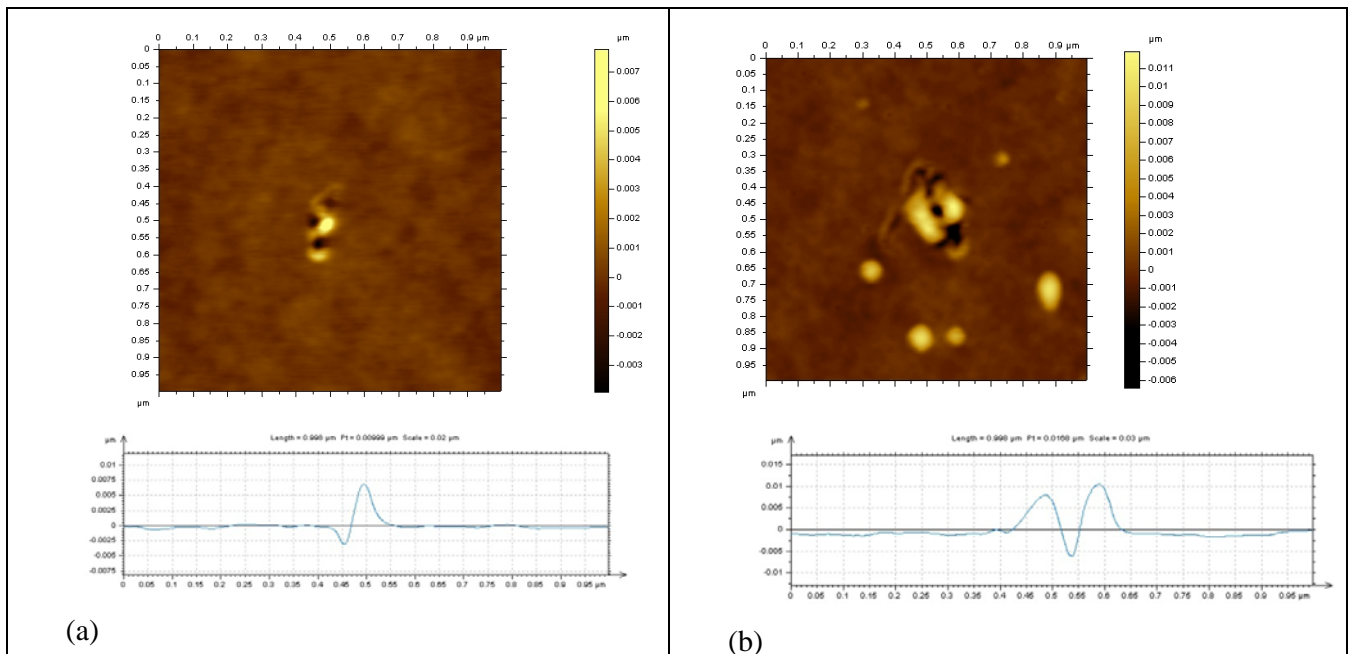


Figure 3. Depth profile of AFM tip indent on top side of PS + G-CNT composite. Indent was obtained at maximum load of 600 nN. CNT concentration (a) 10vol%, (b) 80 vol%.

3.2.2 PS/CNT composite conductivity and self-healing abilities

One of the main goals of the project was to obtain conducting polymer/CNT nanocomposites, that would be able to sense the formation of cracks and heal them before the material failure occurs. Kelvin Force (KFM) and current sensing (CS) AFM were used to measure composite electrical properties. KFM measures the local contact potential difference between a conducting tip and the sample, thereby mapping the work function or surface potential of the sample with high spatial resolution. Initially, this mode was used to characterize the nanoscale electronic properties of metal/semiconductor surfaces and semiconductor devices. Only recently, KFM was applied to organic and biological materials, and therefore is a rather new instrument in the field of polymers and life-science. However, it is very useful to identify electrical properties of conducting/semiconducting nanostructures and their effect on the rest of the device.

We primarily were interested to identify if our nanocomposites were conducting, or if some electrical properties could be measured. Additionally, KFM is using tapping mode of imaging, and so no damage to polymer were supposed to be induced, and therefore, tip interaction with surface did not affected surface morphology and underlying electrical properties. Examples of surface potentials of the top side of our composites are given in Figure 4 for PS/G-CNT 10vol%, and 80 vol%. Nanocomposite containing 10vol% CNTs, had a very smooth surface with all nanotubes hidden beneath top layer, and so no surface potential was recorded. 80 vol% CNT containing composite had a large number of small nanoparticles/nanoclusters, and so resulted in some electrical response.

Most of the nanotubes will be hidden below the surface, and the electrical contact attached to the sample surface, will not be connected to the conducting nanostructures. Therefore, we measured nanocomposite cross-section, where we have expected higher density of conducting CNTs. And so better electrical response, as shown in Figure 5 (more images are given in Appendices 1A and 1B). It is not surprising that composites with 80 vol% CNTs showed the best electrical response. What is interesting however, is the behavior of composite with 10 vol% CNTs under the constant KFM imaging. As shown in topographical images in Figure 5a and Appendix 1A, composite surface has 2 layers and large nanoclusters of what we expect to be nanotubes. The presence of the layers is due to the shaving of the surfaces with microtome, as no other additional preparation was performed. Similar morphology was also observed under optical microscope as shown in Figure 2b, and at higher magnification in Figure 6. After, several AFM scans on the same area, it was notices that top layer started to disappear, almost like melting-away (see Appendix 1A). This phenomenon was observed every time when prolonged scanning was used. What is the reason behind it, is not clear yet. It will be further investigated in an independant project, as the phenomenon was accidently found and present grant just finished. No difference in surface morphology was noticed on 80 vol% CNT containing samples.

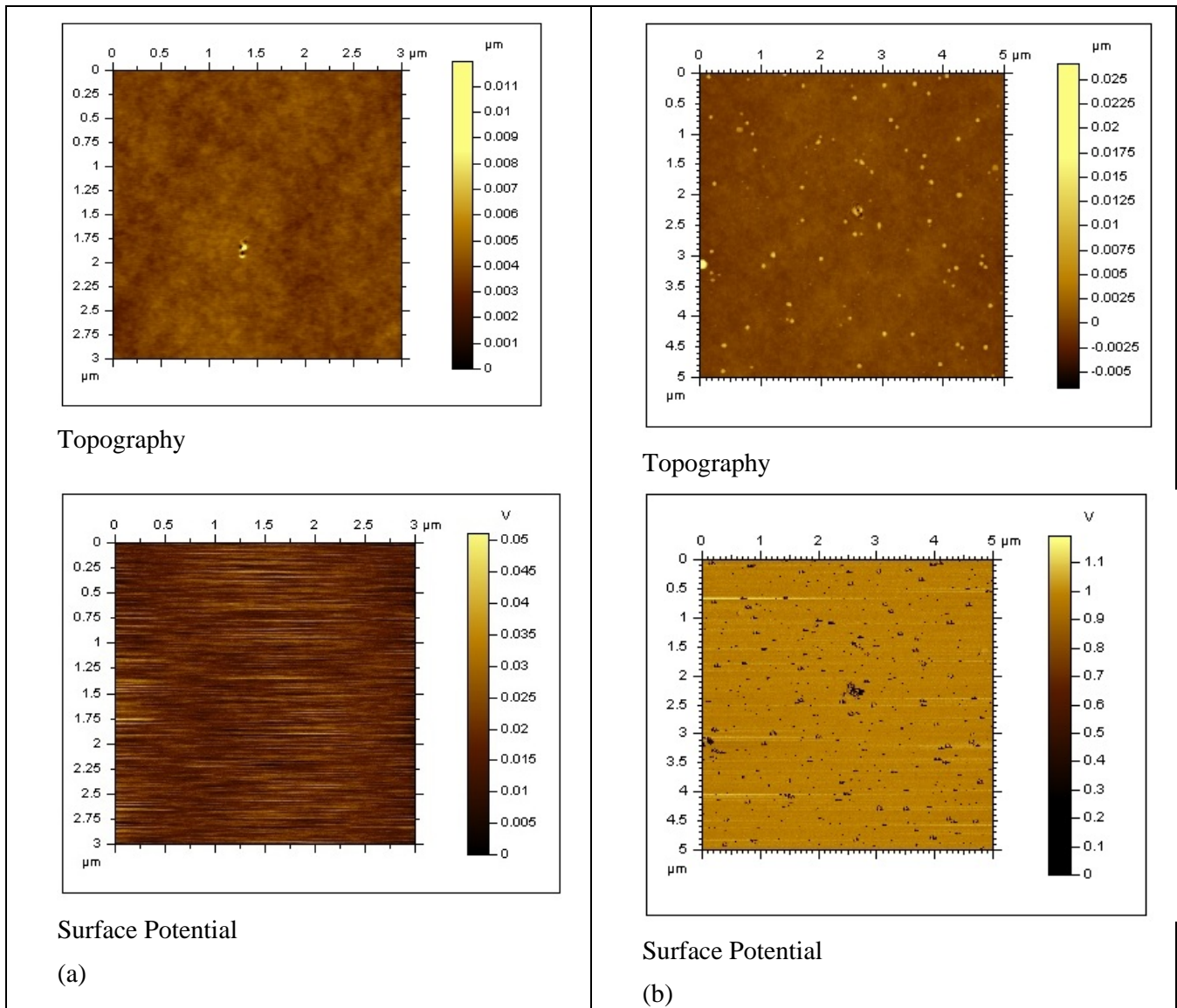


Figure 4. AFM images of the top side of PS + G-CNT using Kelvin Force Microscopy. (a) 10 vol%, (b) 80 vol%.

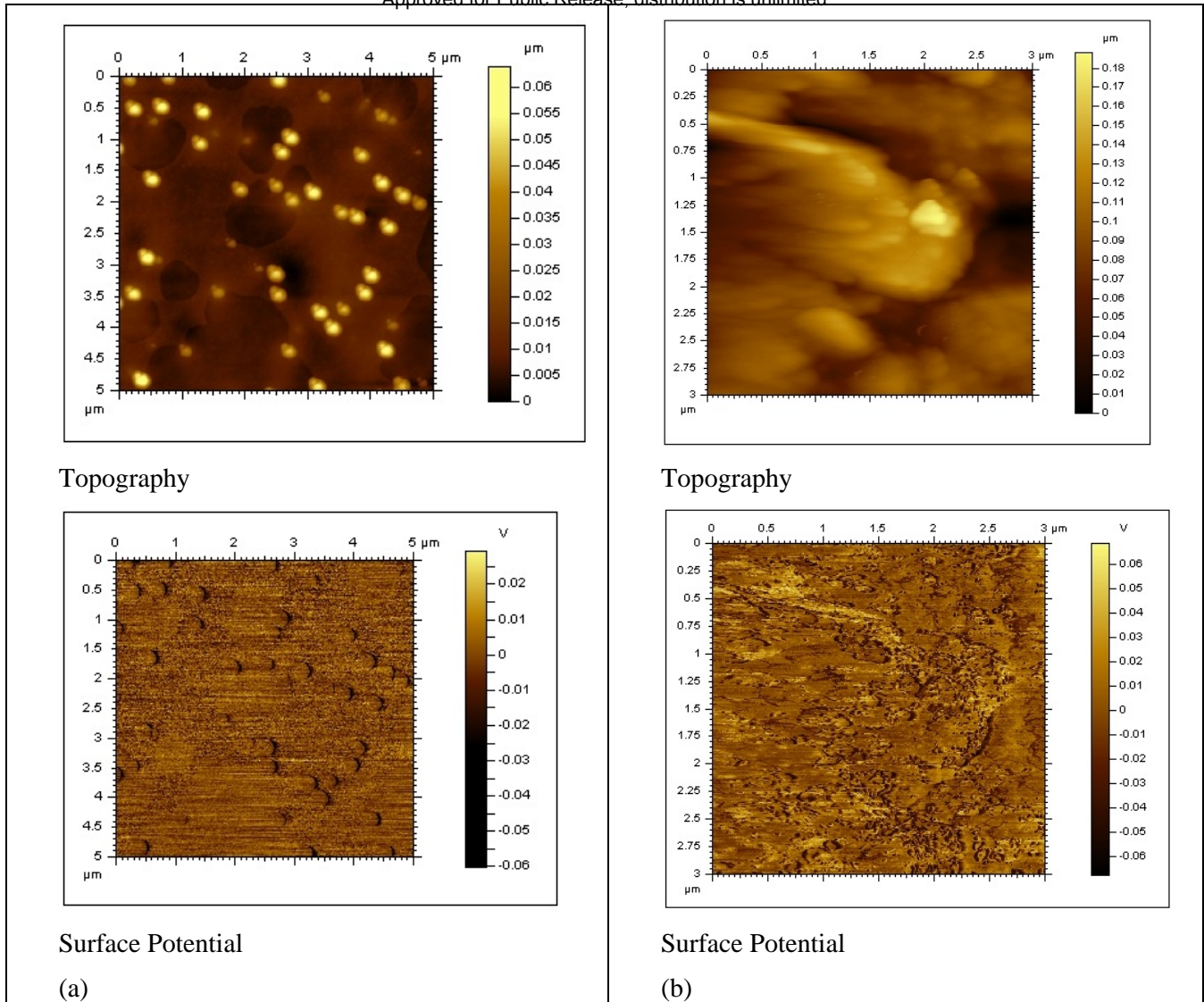


Figure 5. AFM images of the cross-section of PS + G-CNT using Kelvin Force Microscopy. (a) 10 vol%, (b) 80 vol%.

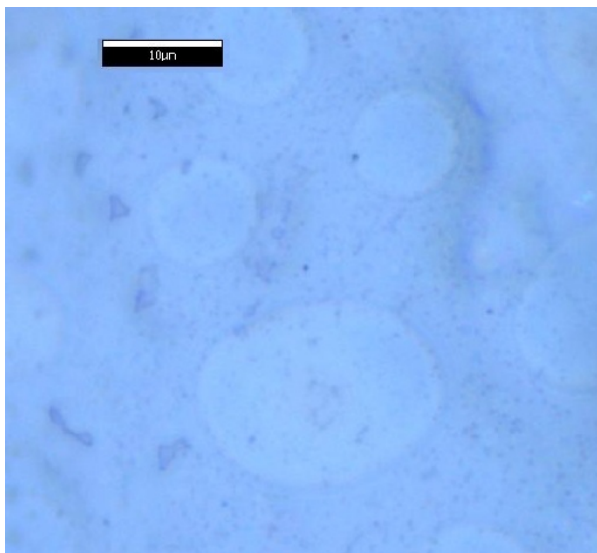


Figure 6. PS + G-CNT 10 vol%.

As composite cross-sections showed the best electrical properties, we further investigated them using Current Sensing (CS) AFM. The following discussion will be addressed to PS + G-CNT 80 vol% nanocomposite. CS AFM images for PS + G-CNT 10 vol% are attached in Appendix 2A.

As mentioned in earlier report, CS-AFM is a powerful technique for electrical characterization of conductivity variation in resistive samples. It allows direct and simultaneous visualization of the topography and current distribution of a sample. By applying a voltage bias between the substrate and conducting cantilever that is constantly in contact with the sample, a current flow is generated. We expect, that generated current flow will be enough to heat the sample locally to trigger polymer chain mobility and reorientation to promote “self-healing”.

Figure 7 shows Topographical, friction and current sensing AFM images and corresponding profiles for PS + G-CNT 80 vol%, when 5V sample bias is applied. Small current between 0.2 – 1.3 nA is measured. After the sample was scanned 8 times (total scanning time ~ 60 min), we observed slightly different results, as shown in Figure 8. The features in topographical images became more clear, while measured current is reduced to pA, and it is difficult to differentiate features that were seen in initial map. The drop in current values can be explained by the formation of the insulation layer on top of the surface. Another reason that cannot be excluded, is the contamination of the tip with thin layer of PS, that acts as additional insulator. But if this were the case most of the features shown in topography would have become blur or increased in size due to enhanced tip radius. This however was not the case, as some features became sharper (compare topographical images in Figures 7 and 8). Therefore, most likely explanation is that sample was slightly heated while tip was passing the surface. It resulted in polymer chain reorientation and enhanced movement.

To check if “healing” could be induced by passing current through the tip to the sample, a scratch of ~ 1.5 μm in length was made on the sample surface using AFM tip, at load of 600 nN, Figure 9. After the prolonged scanning of 60 min, the topography has changed, and scratch depth was reduced by 1 – 1.5 nm (Figure 9b). Appendix 2B includes more images of topography, friction, CS and their respective profiles at the same place at different image acquisition times. The scratch might disappear completely at prolonged scanning, although if insulation layer is formed on the surface (as observed in the drop of current maps) that might take longer than expected. Nevertheless, the concept of polymer composite self-healing by passing the current through the sample was proved. Providing nanotube network is uniformly generated within the matrix, and electrical contacts are directly connected to the CNTs, full healing could be obtained much faster. Recent findings result into the new/extended project, where I intend to use the network of conducting nanofibre composites prepared by electrospinning.

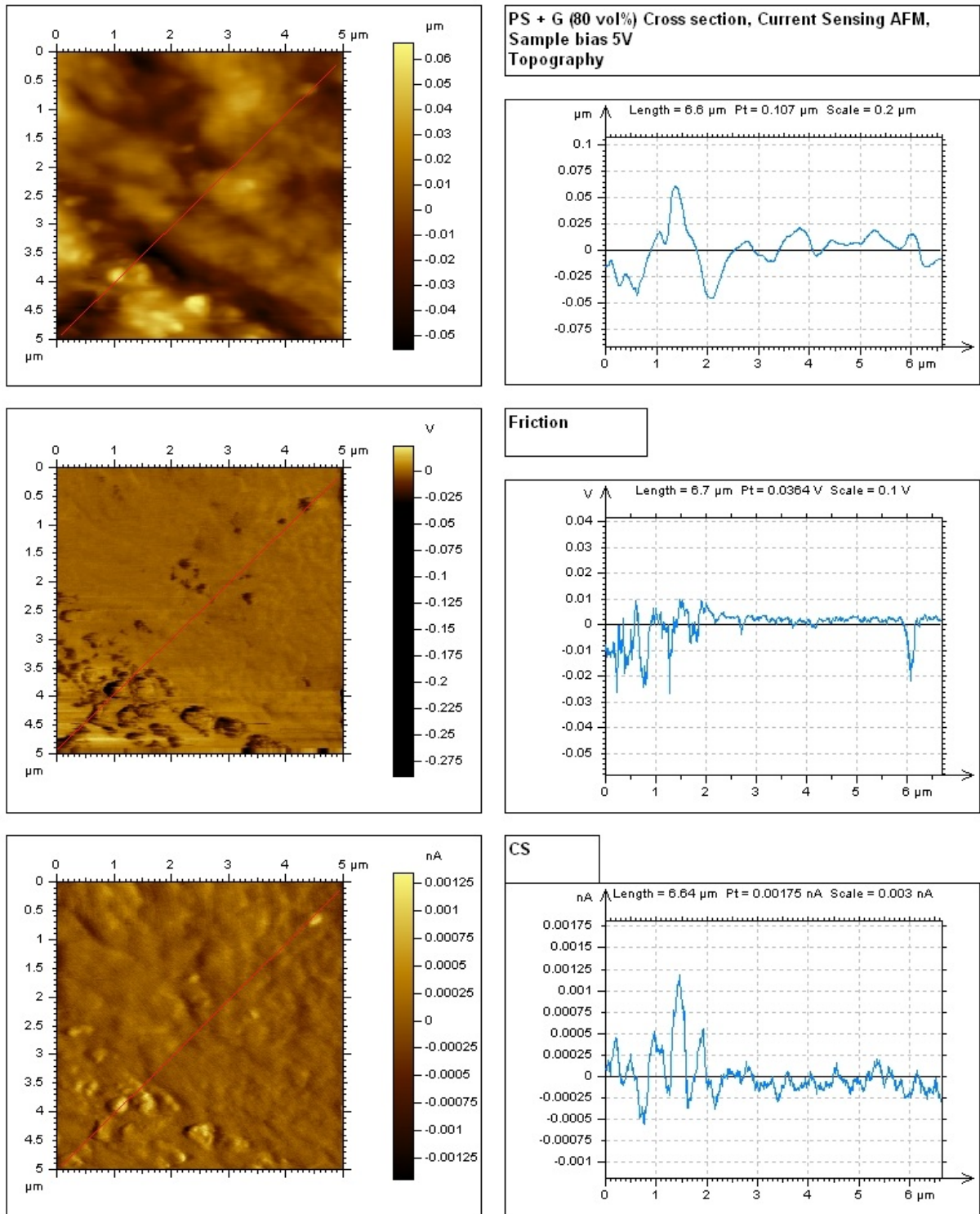
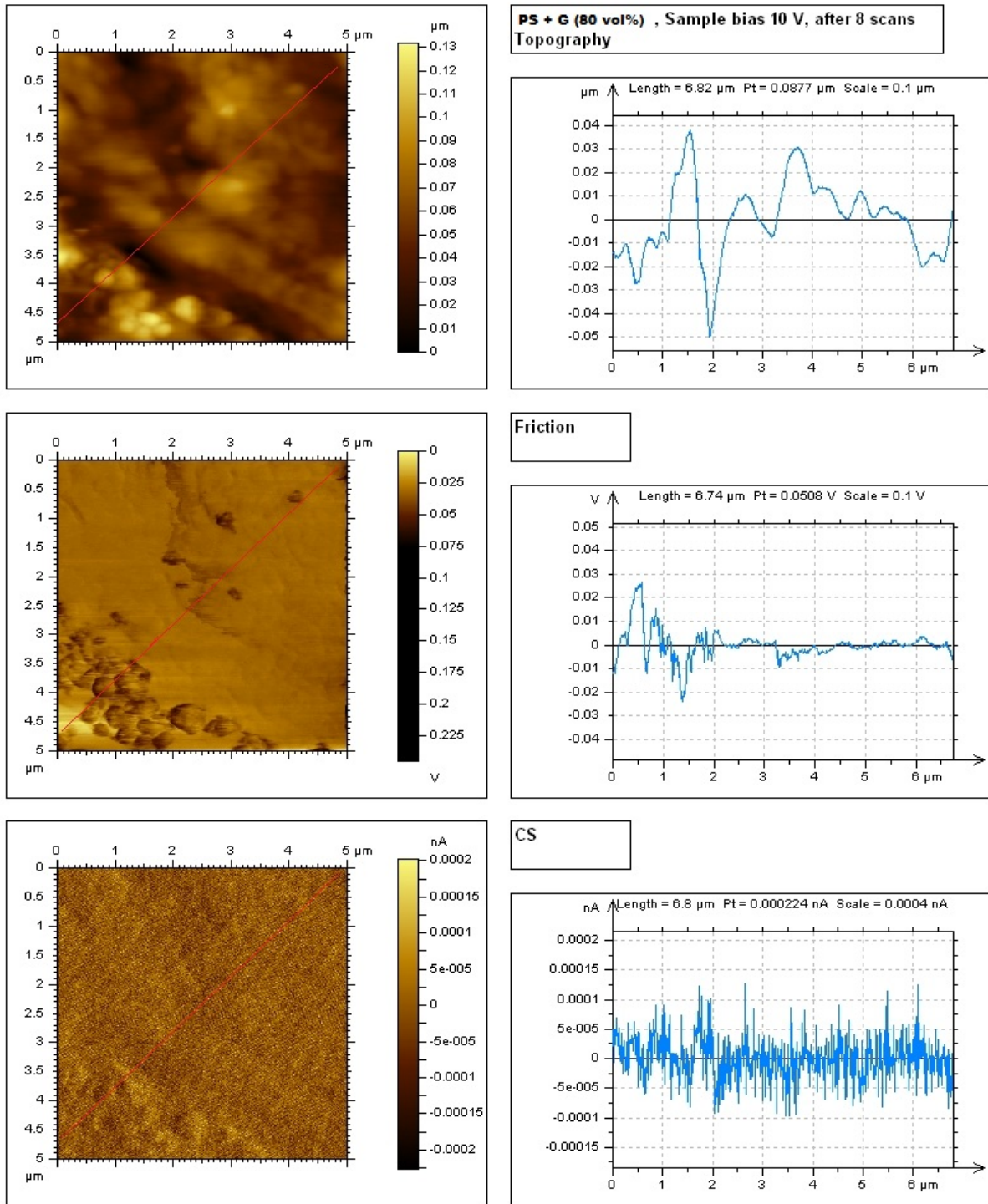


Figure 7. 1st scan of Current Sensing AFM for PS + G-CNT 80 vol%



Pico Image Basic 5.1.1.5944

Figure 8. Final (8th) scan of Current Sensing AFM for PS + G-CNT 80 vol%.

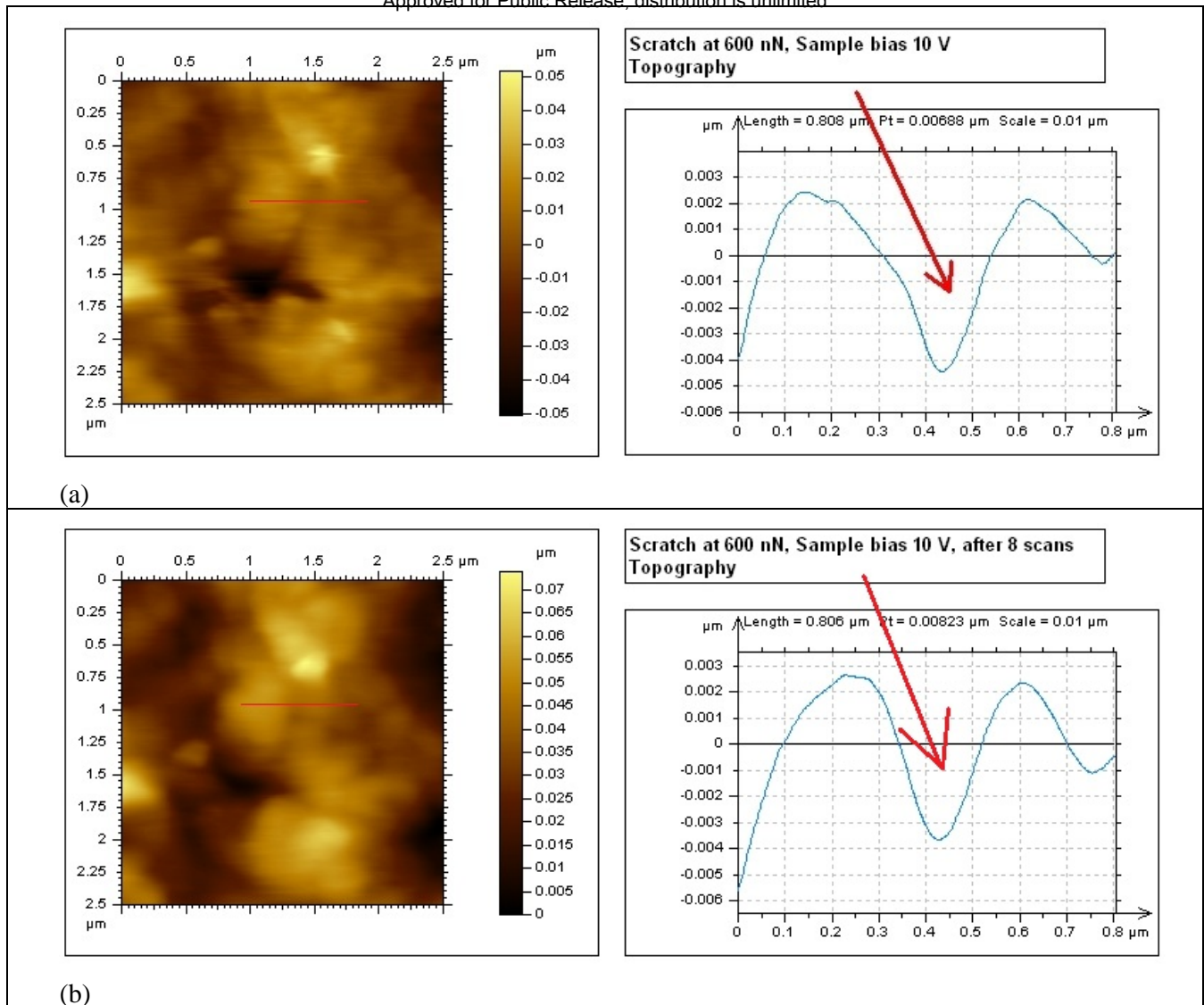
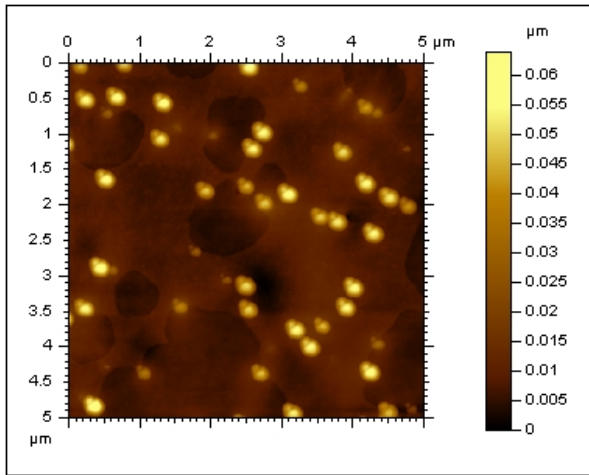


Figure 9. Self-healing abilities of PS + G-CNT 80 vol% nanocomposite, after multiple scanning of the same region. (a) First scan after scratch was done, (b) resulted image after 60 min scanning.

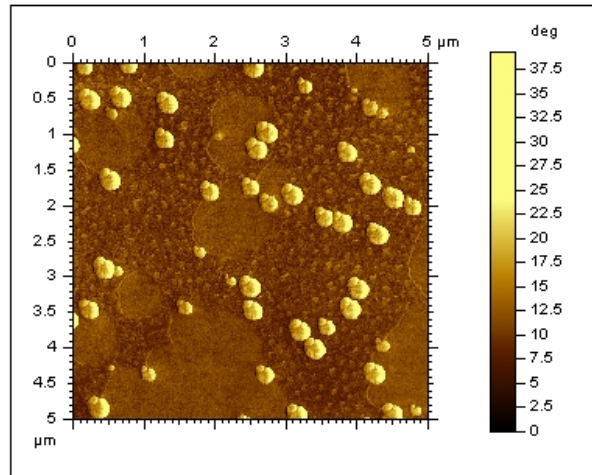
4. Summary of present report

In this section the summary is given for the progress that was made in the last 3 months of the project. We have reported improved carbon nanotube dispersion in solutions using various steps of filtering, sonication and stirring. These CNT solution preparation steps ensured better CNT distribution within polymer matrix. Composite electrical properties were measured using advances AFM modes. Sample conductivity greatly depended on CNT concentration in polymer. The concept of polymer composite self-healing by passing the current through the sample was proved. The research paper is in preparation and should be submitted to scientific journal as soon as it will be finished. The latest work generated interesting results and new ideas for at least 2-3 new projects.

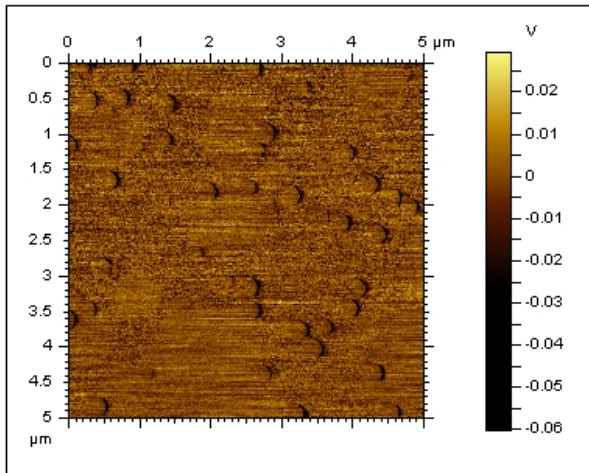
PS + G (10 vol%), Cross-section, KFM-FM
Topography



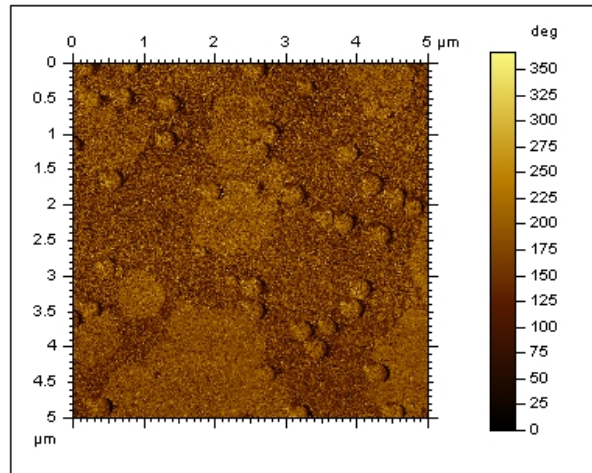
Phase



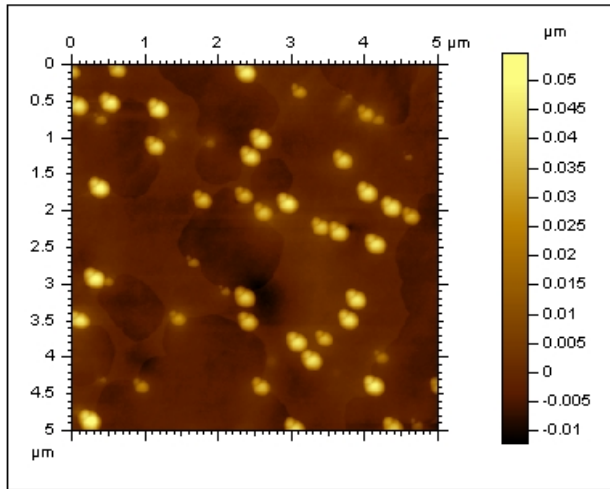
Surface potential



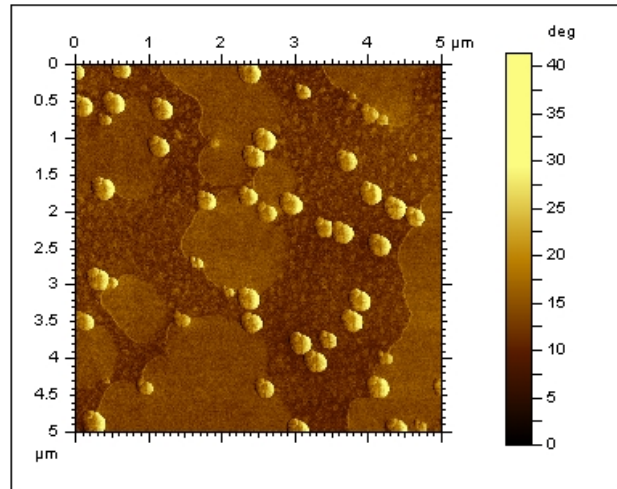
KFM Phase



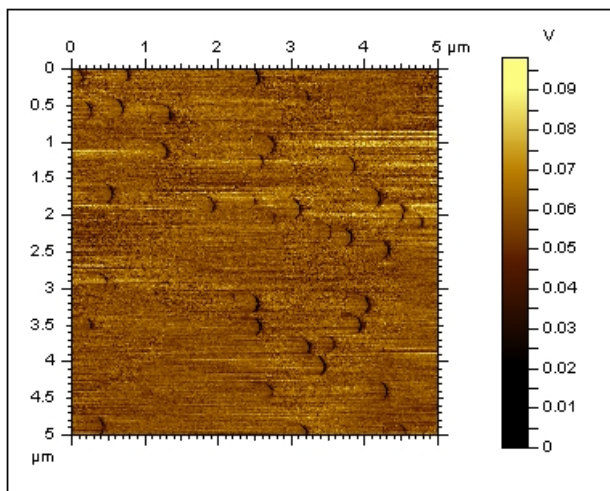
PS + G (10 vol%), Cross-section, KFM-FM, after 6 scans
Topography



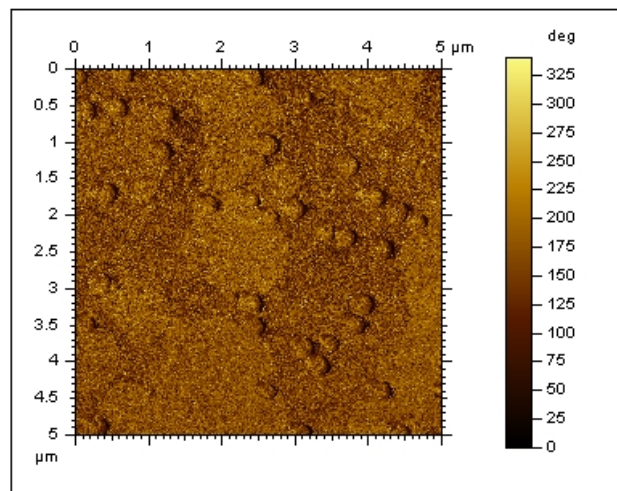
Phase



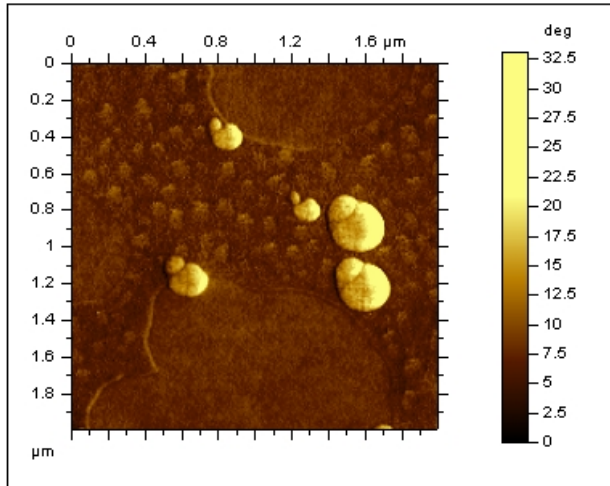
Surface Potential



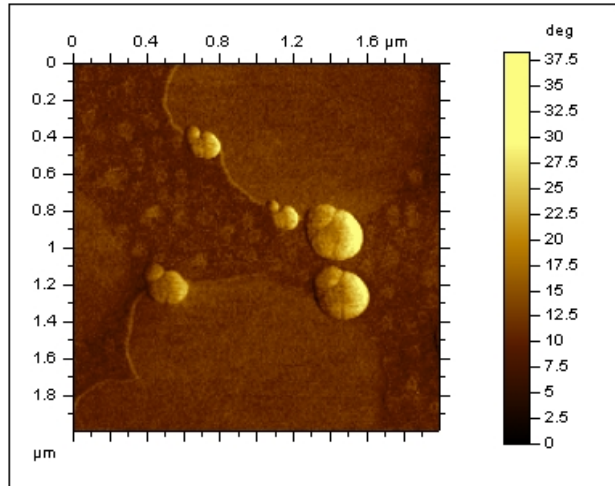
KFM Phase



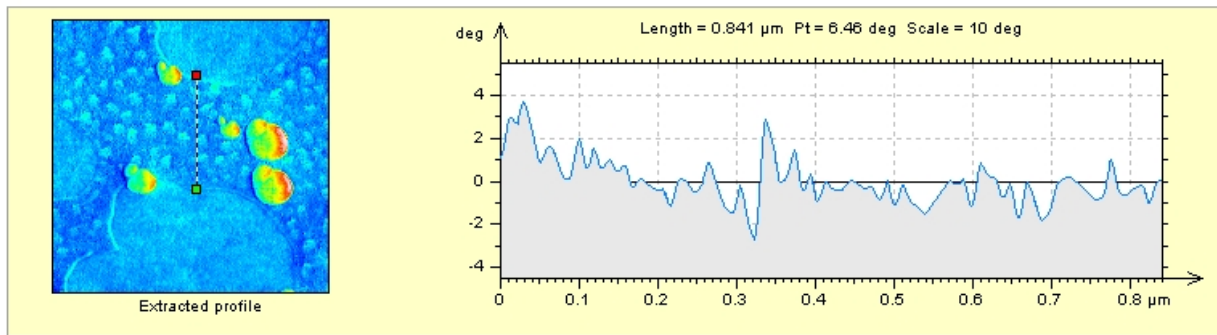
1st scan



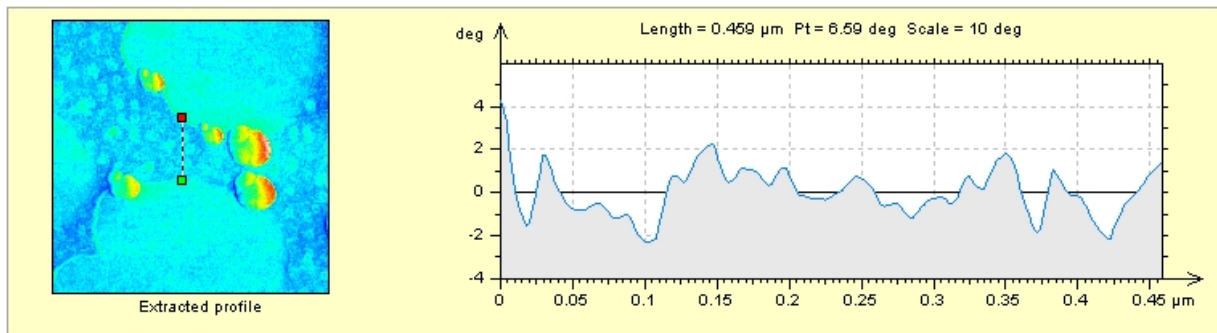
6th scan



1st scan



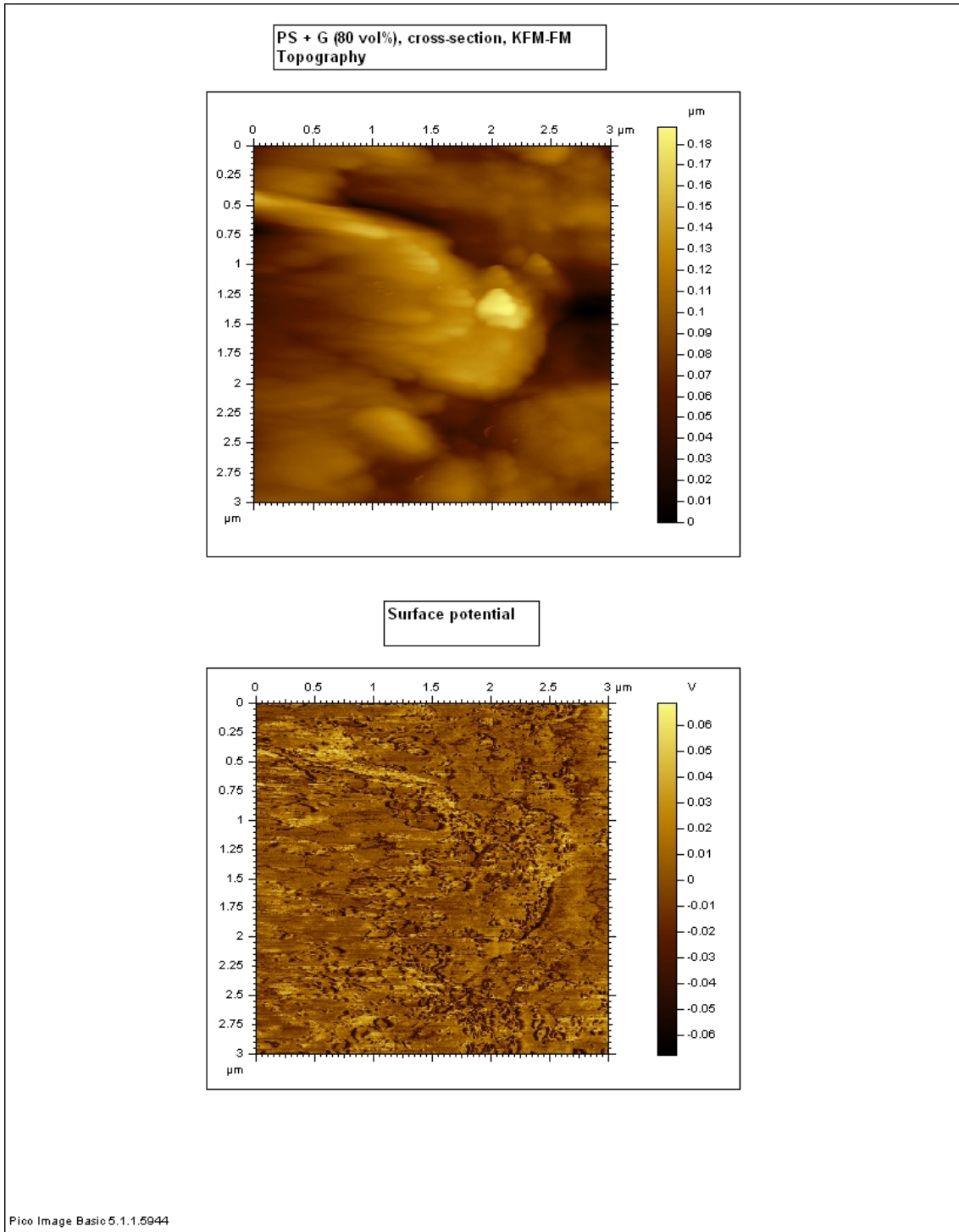
6th scan

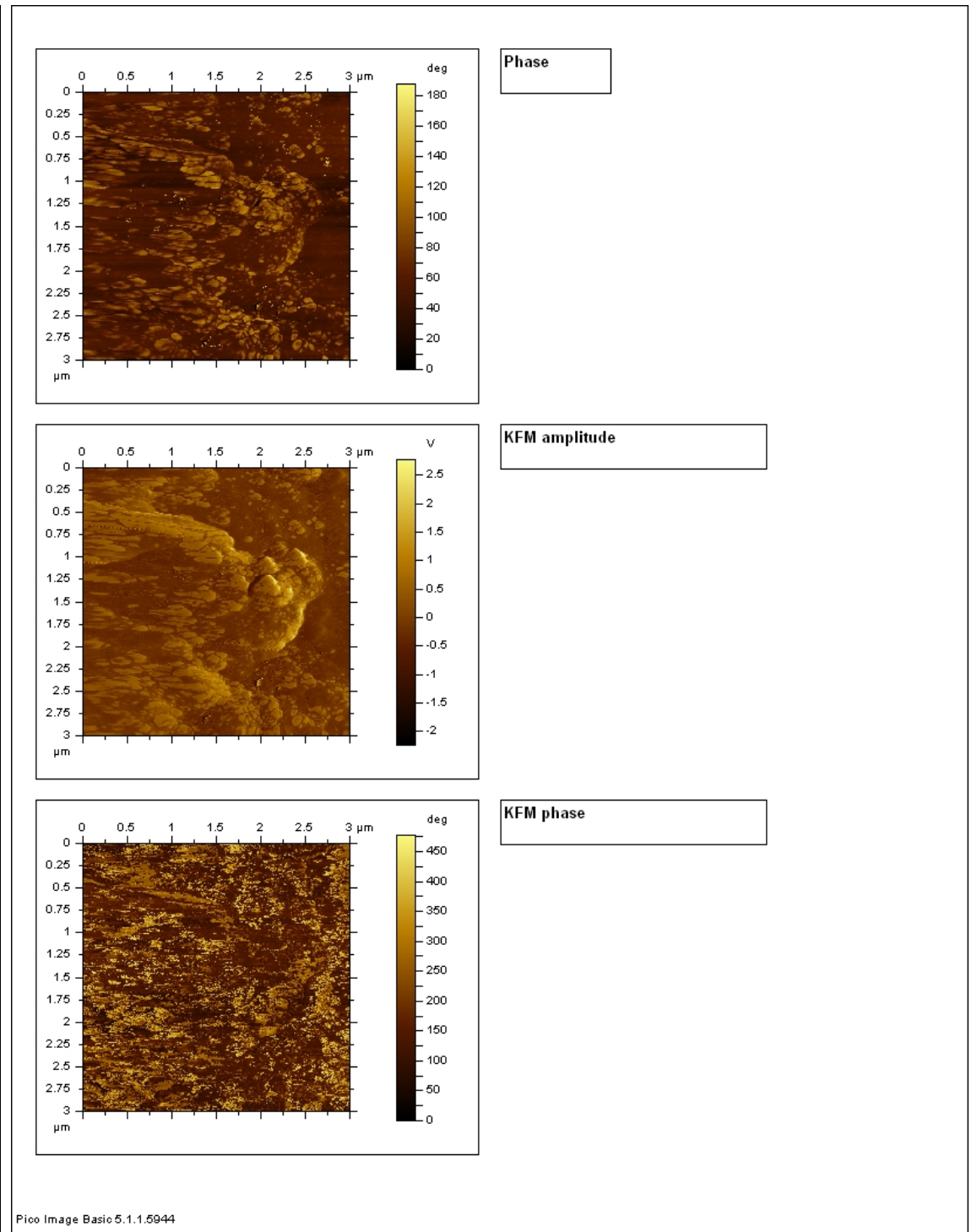


Pico Image Basic 5.1.1.5944

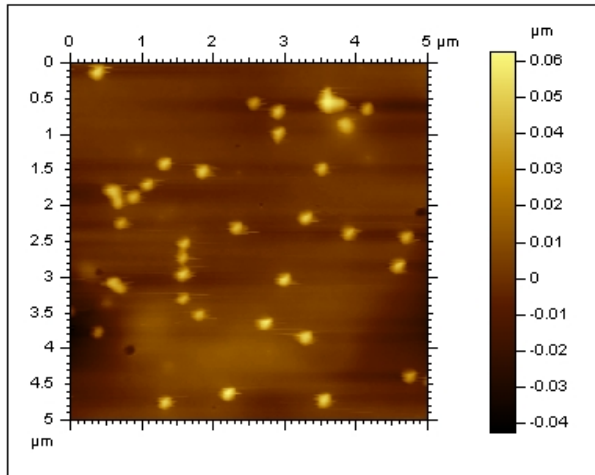
Please note how the top layer of the polymer matrix "melted" with every scan. The width of the top layer was reduced from 850 nm to 450nm.

Appendix 1B

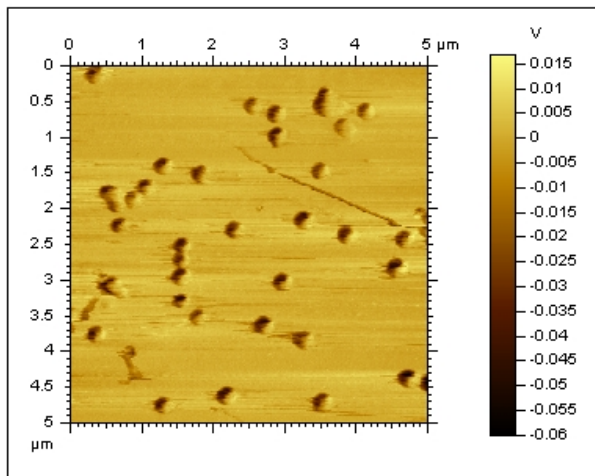
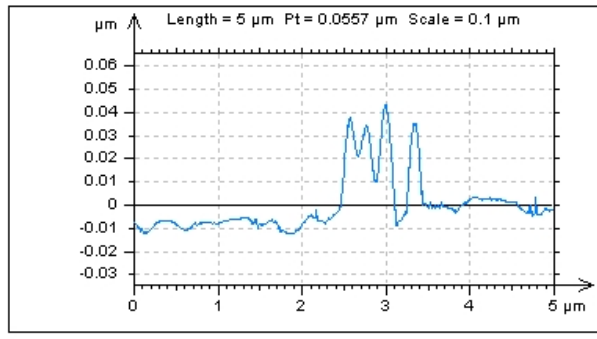




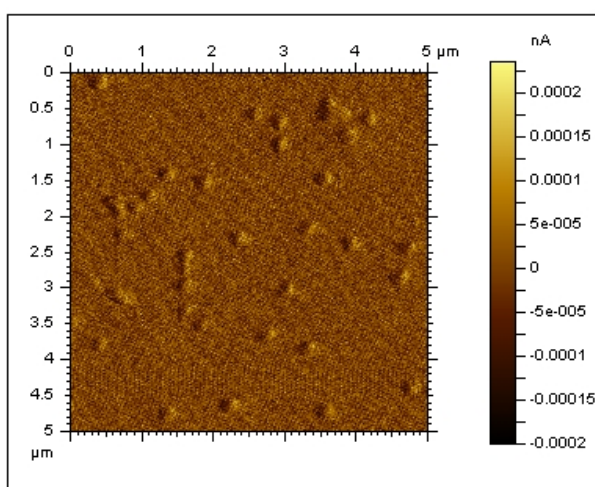
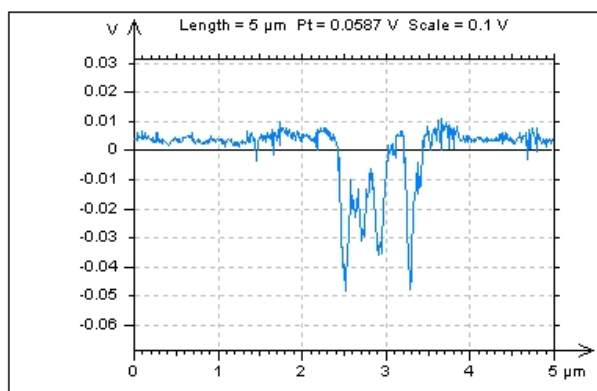
Appendix 2A



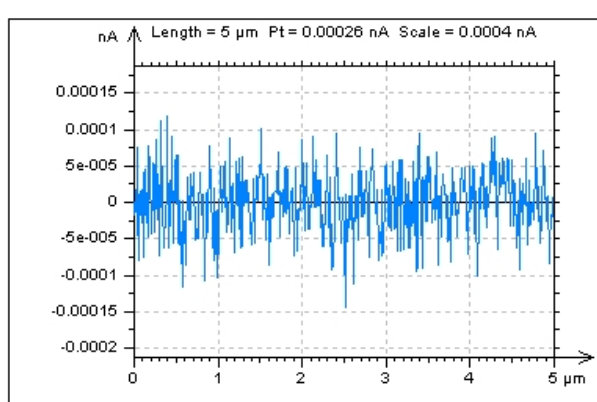
PS + G (10 vol%), cross-section, Current sensing AFM, Topography

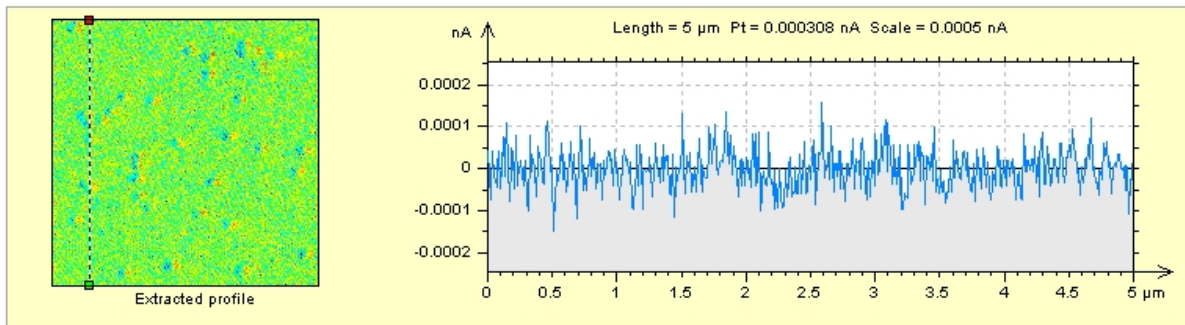
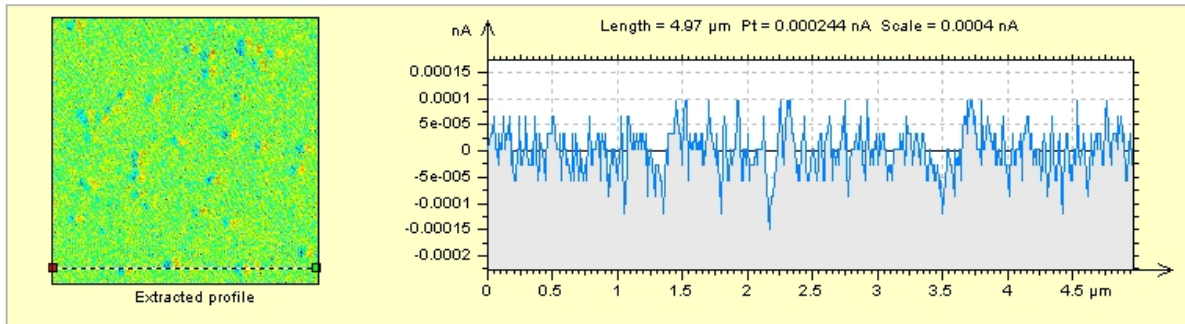
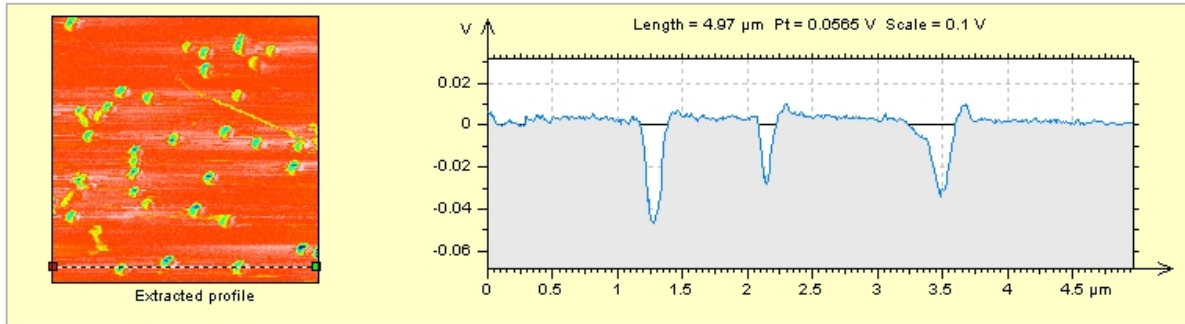
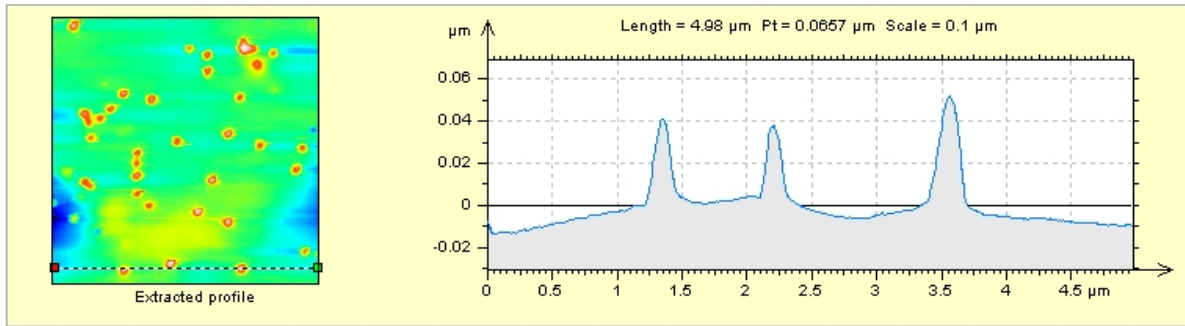


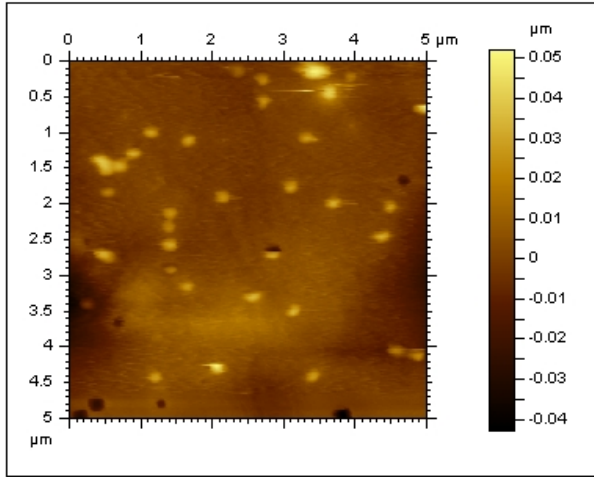
Friction



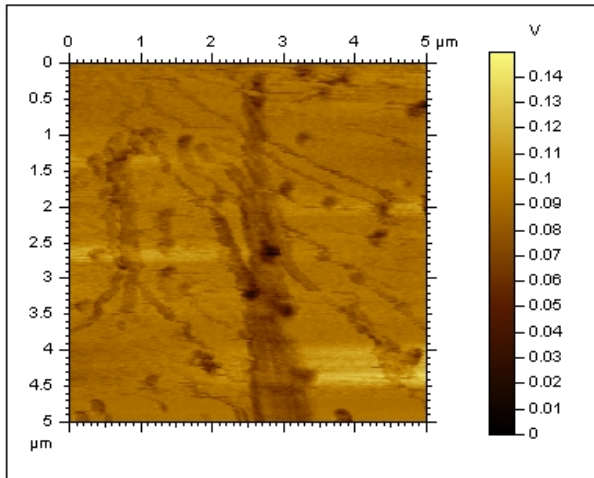
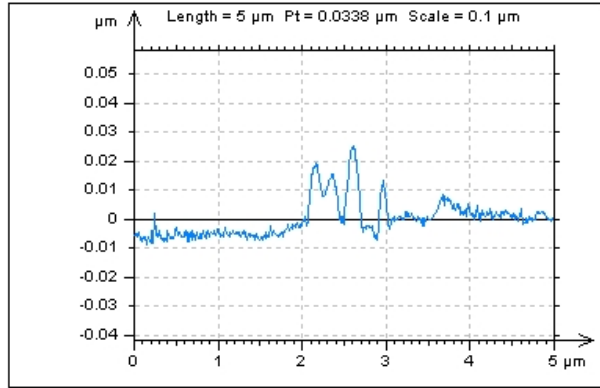
CS



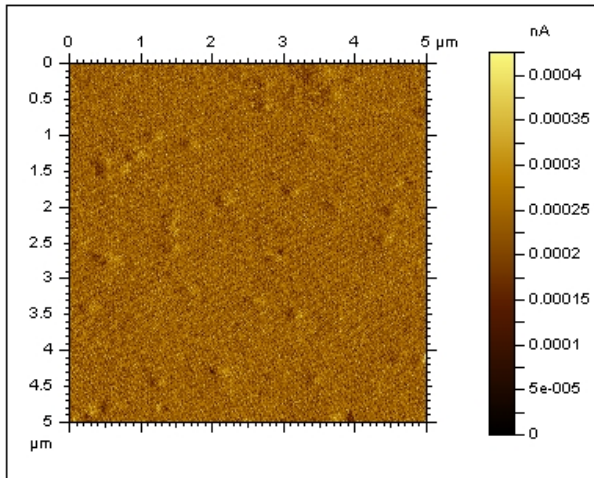
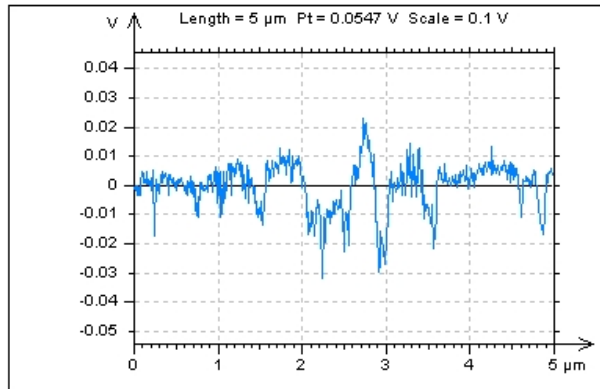




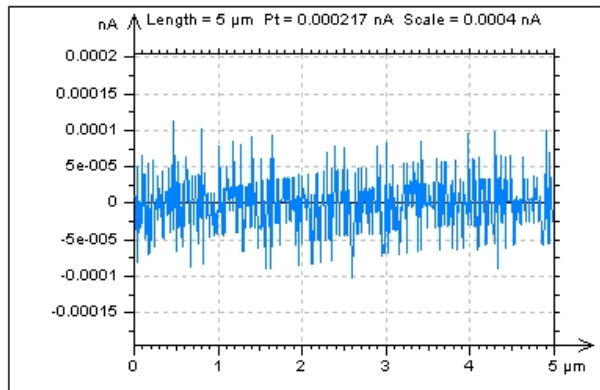
PS + G (10 vol%), cross-section, Current sensing AFM, Sample Bias 10V, Topography

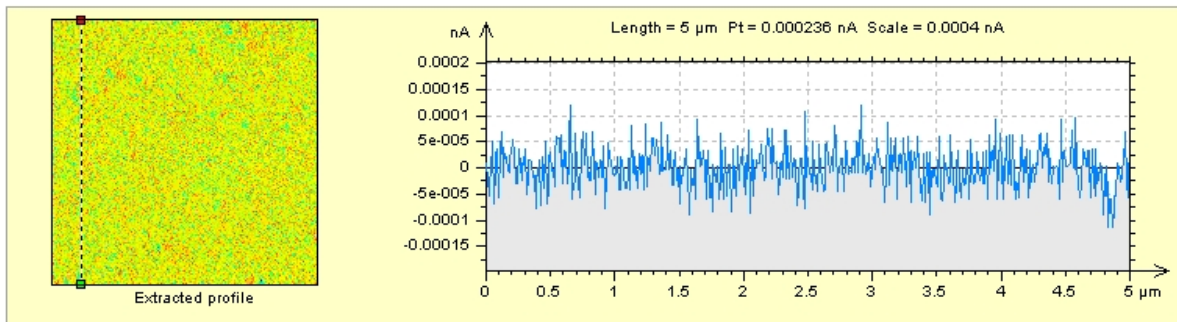
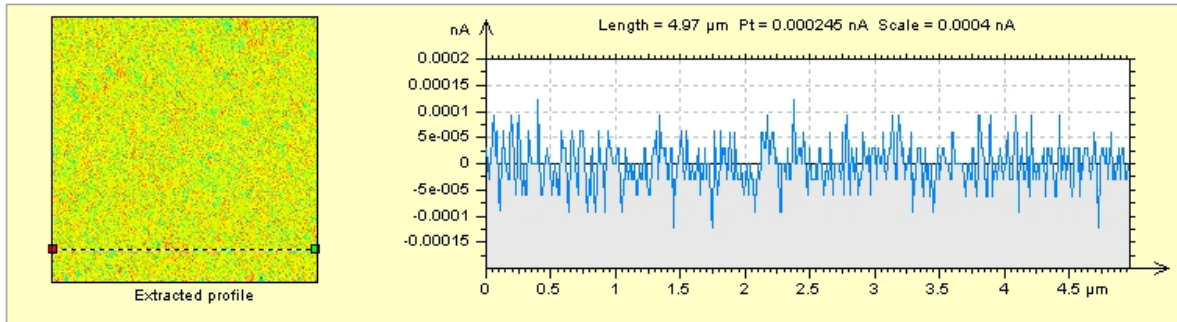
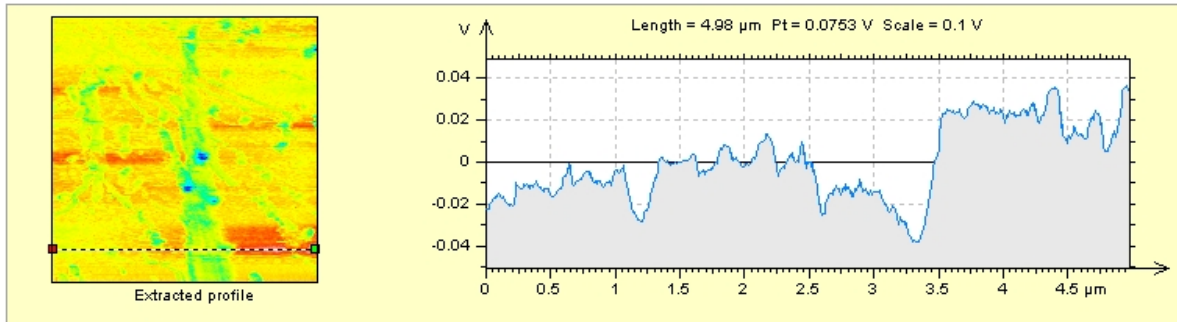
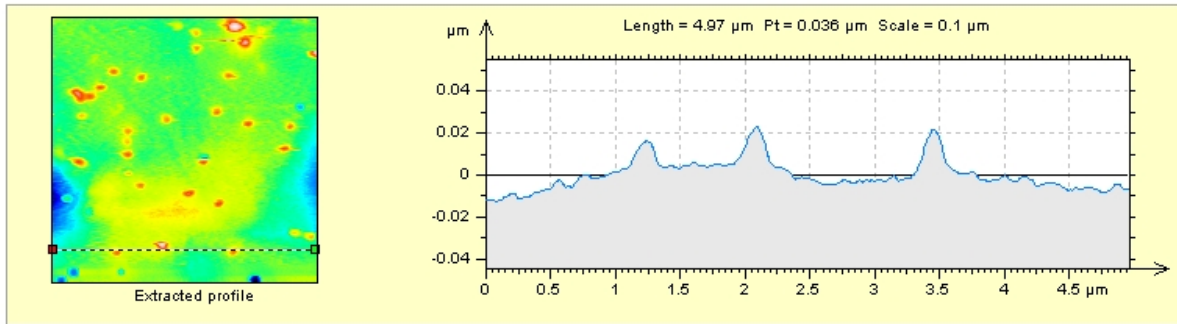


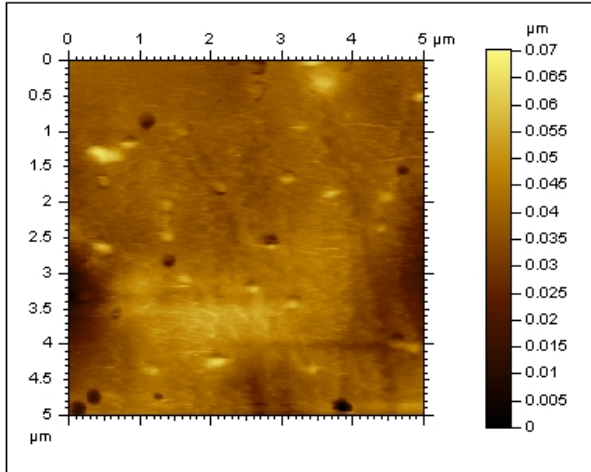
Friction



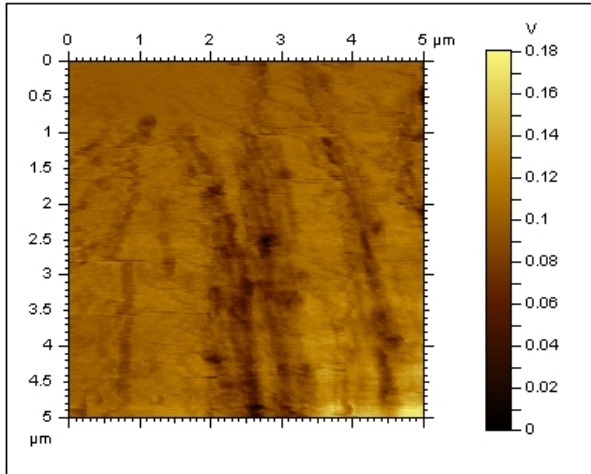
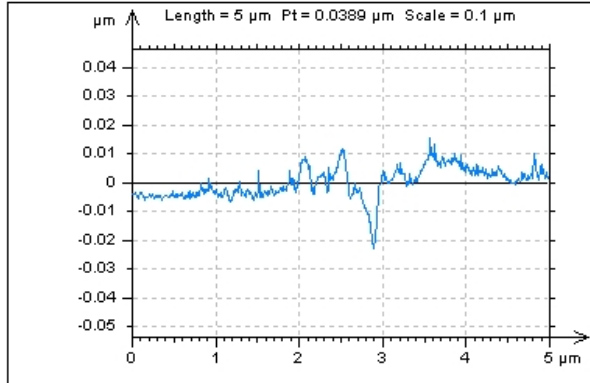
CS



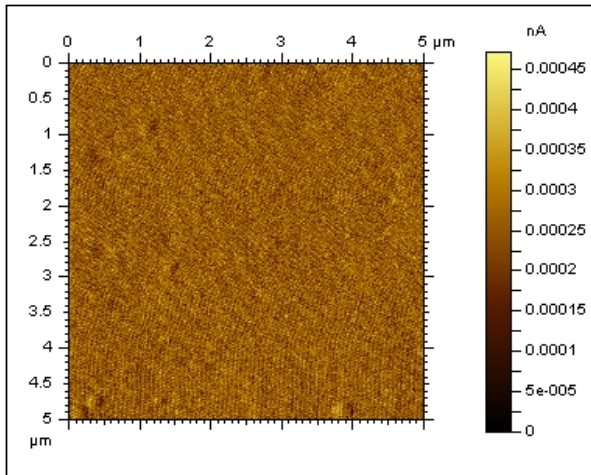
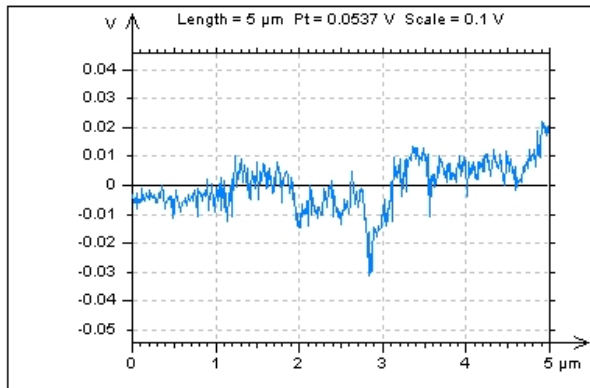




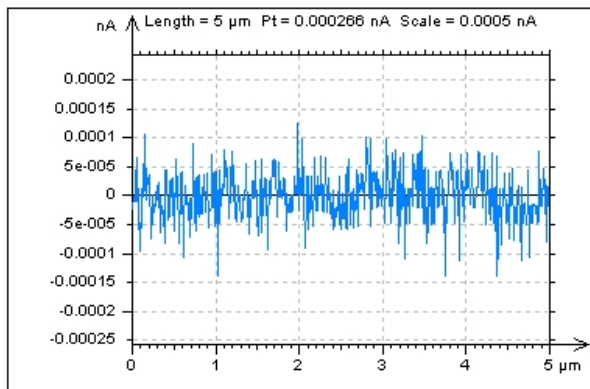
Sample Bias 10V, Scan 5
Topography

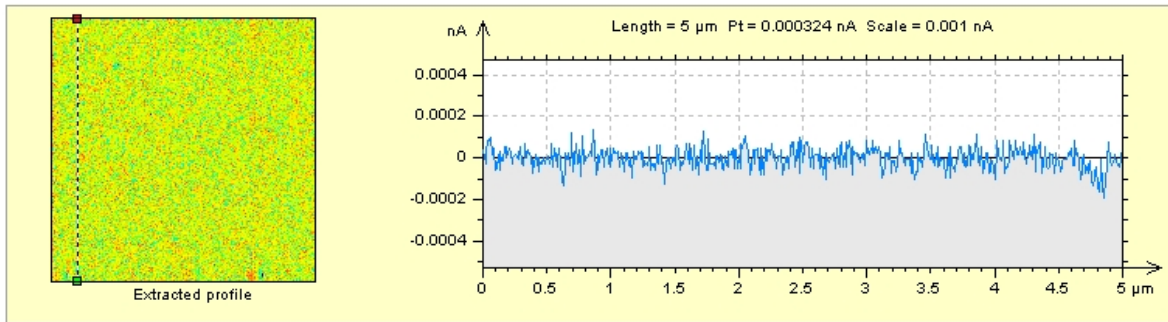
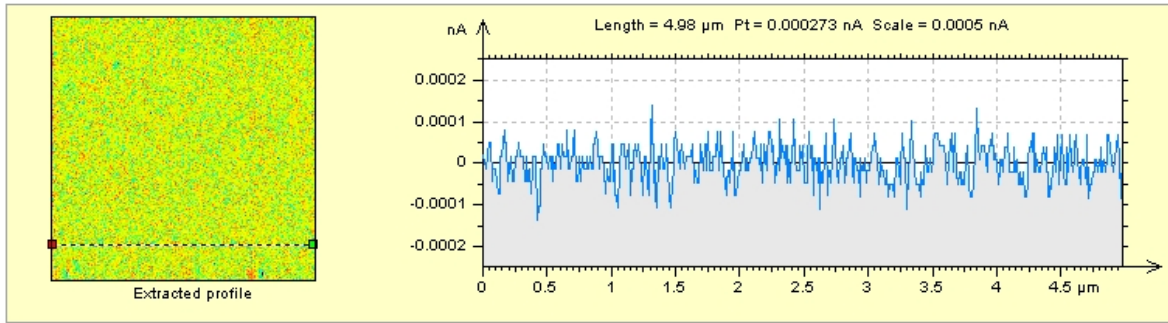
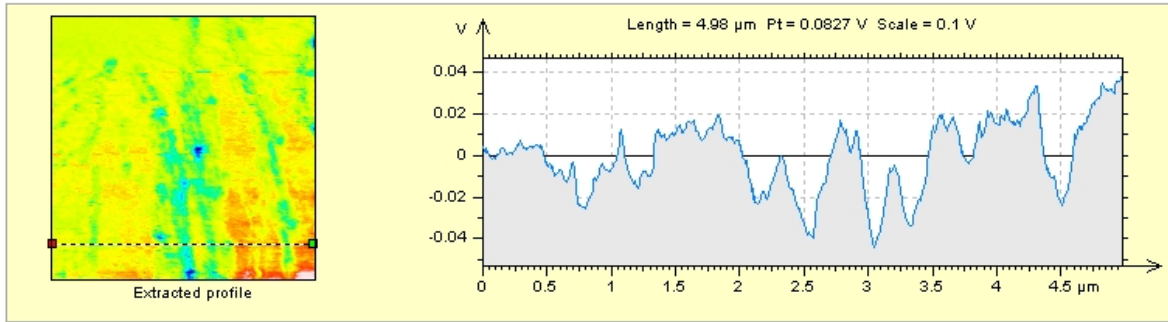
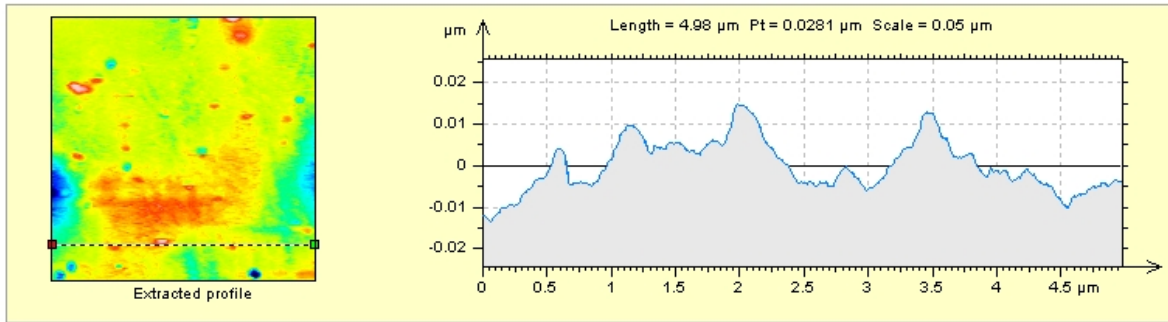


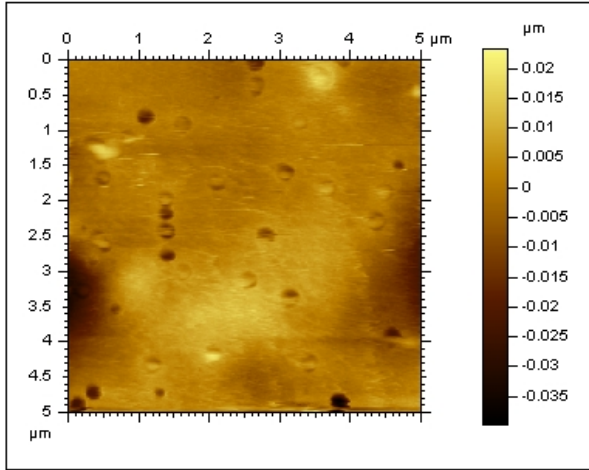
Friction



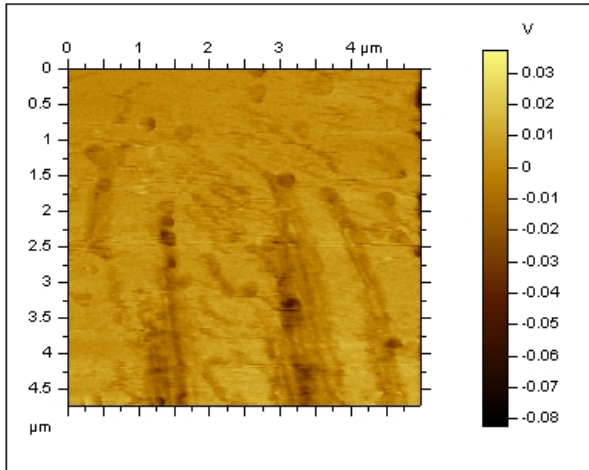
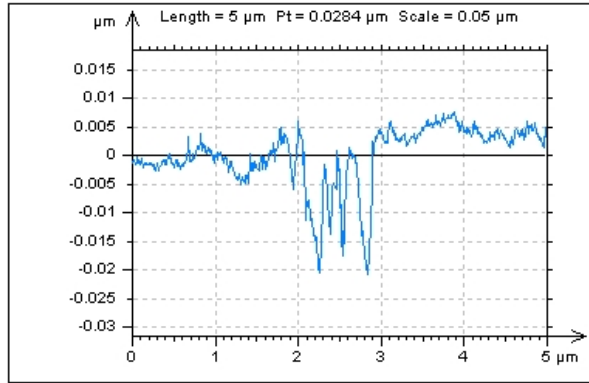
CS



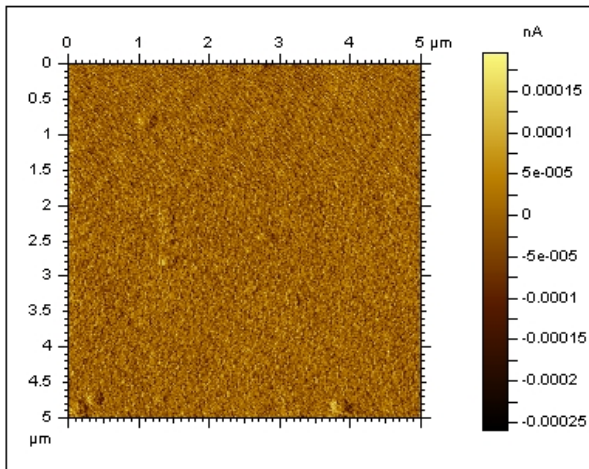
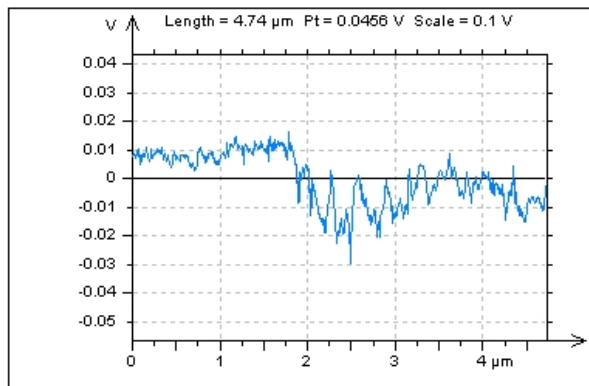




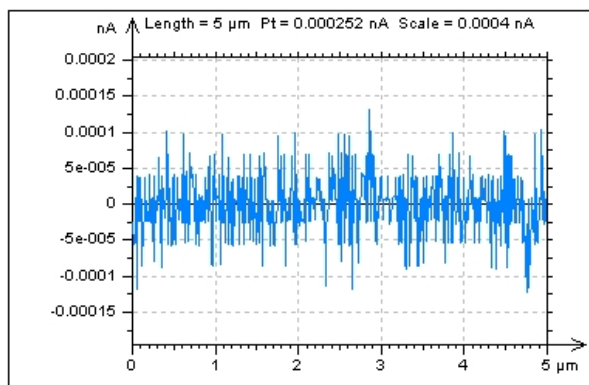
Sample Bias 10V, Scan 7
Topography

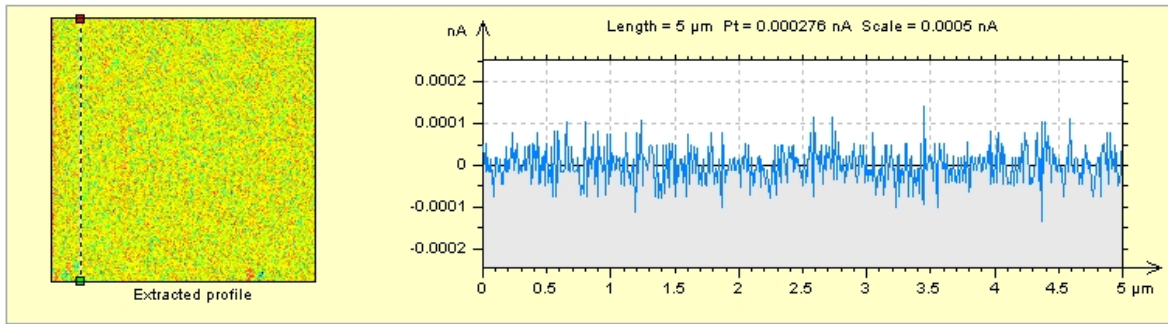
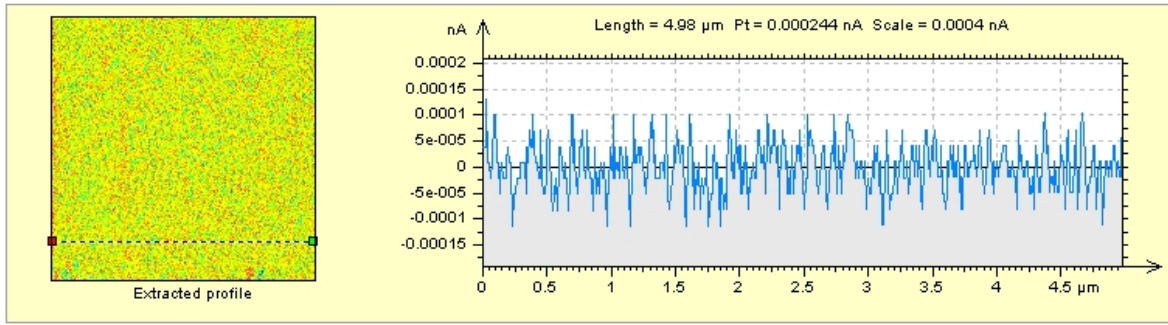
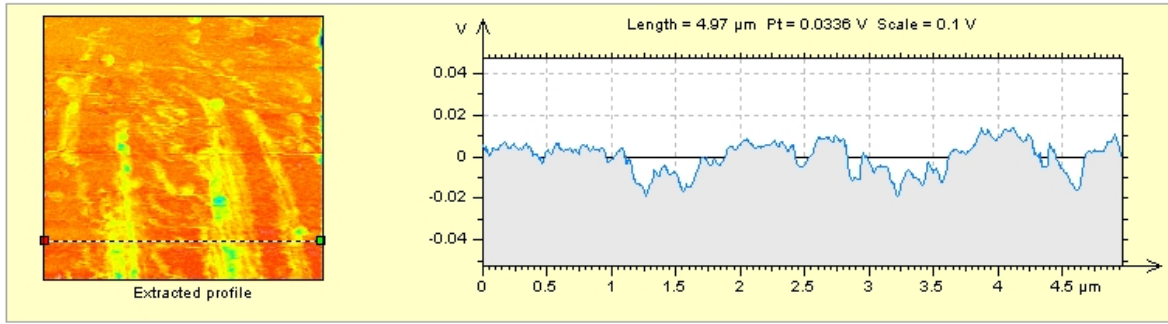
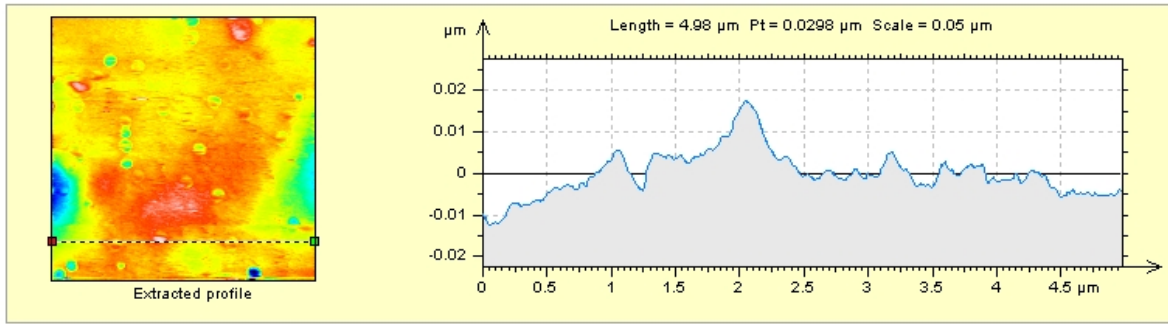


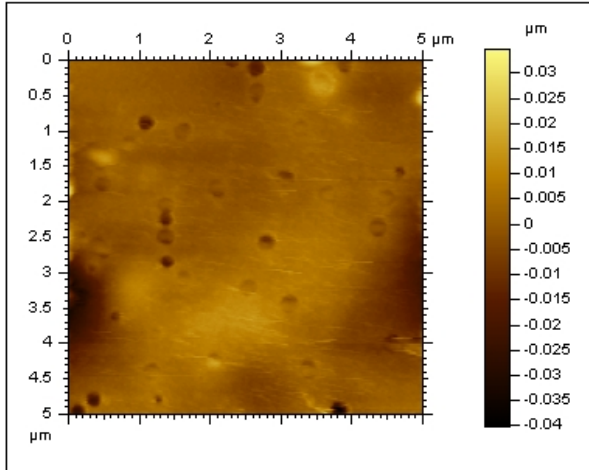
Friction



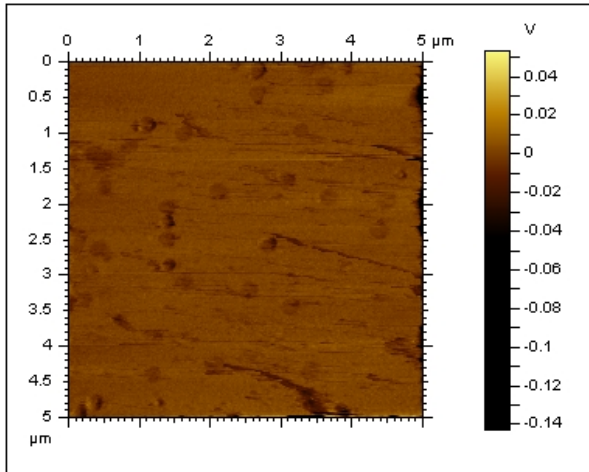
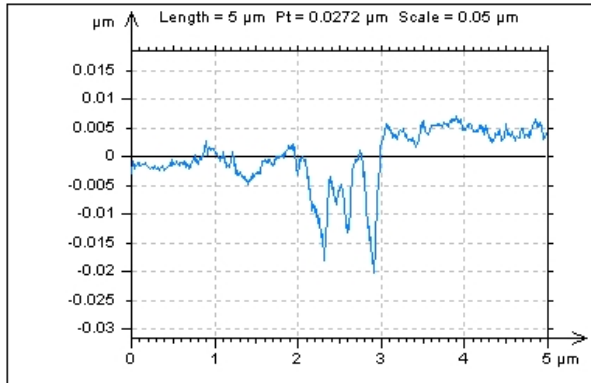
CS



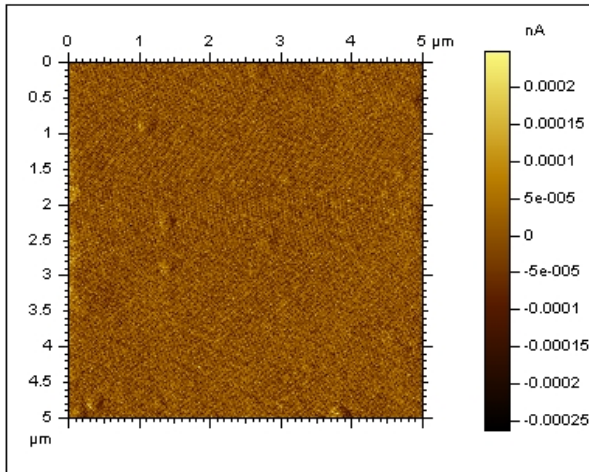
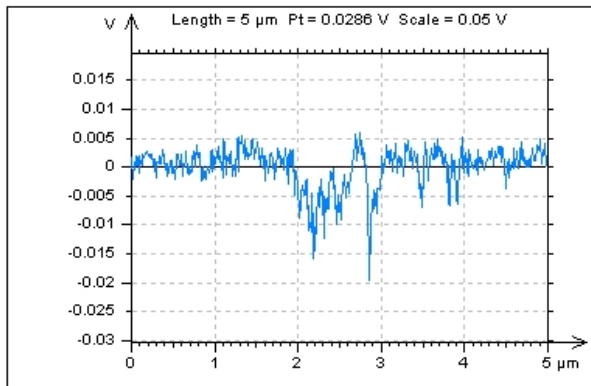




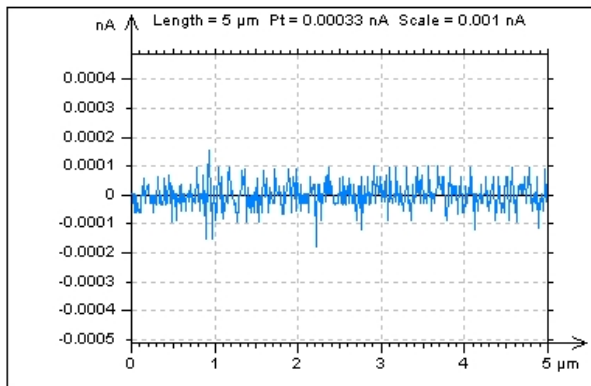
Sample Bias 10V, Scan 7
Topography

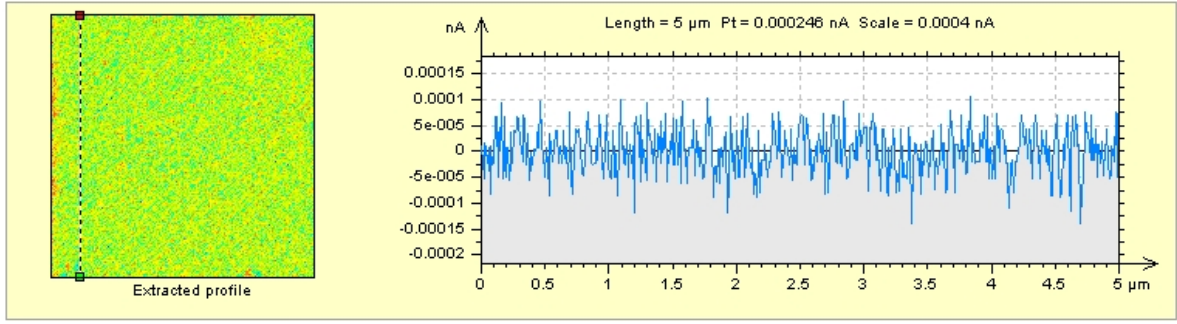
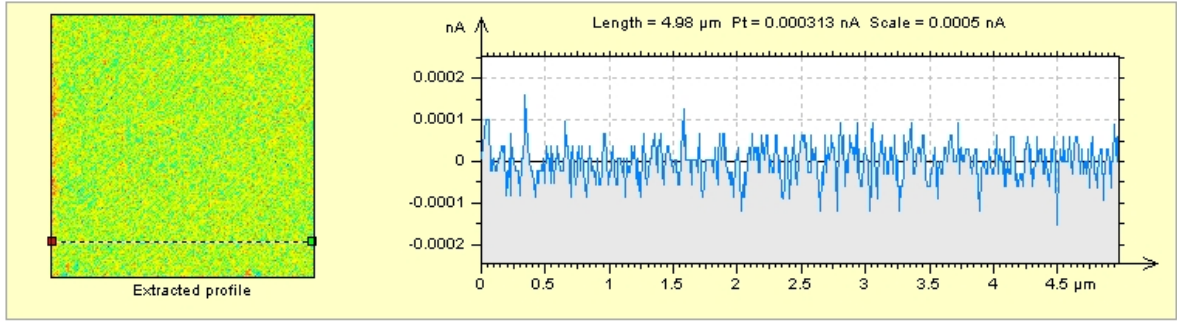
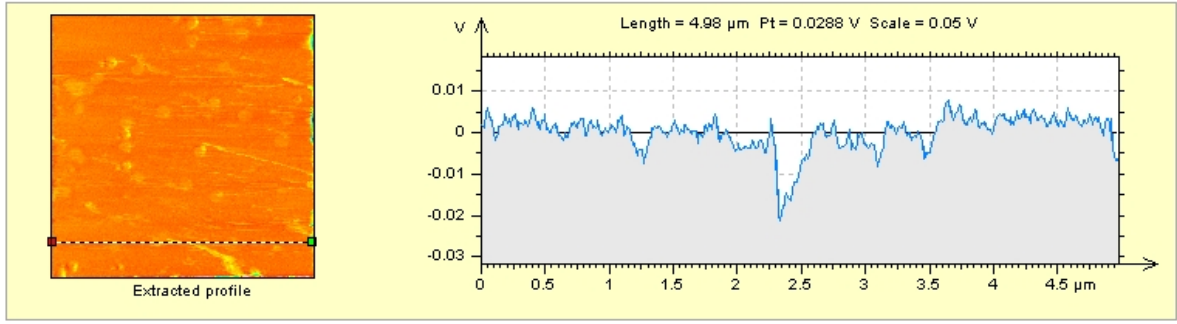
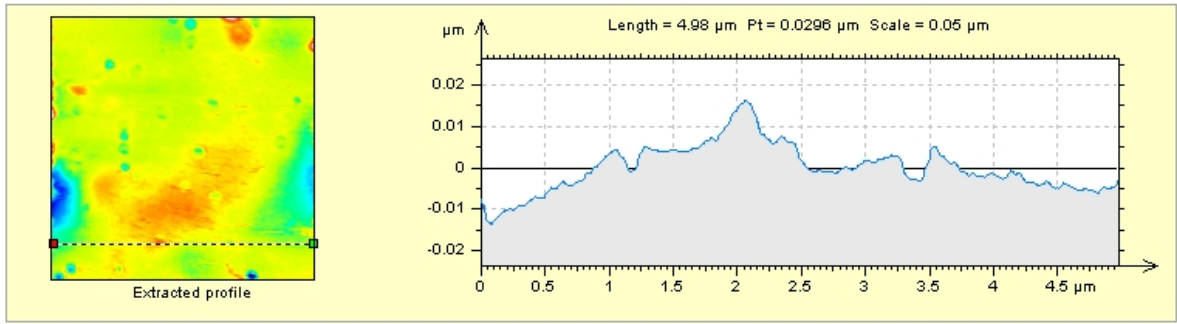


Friction

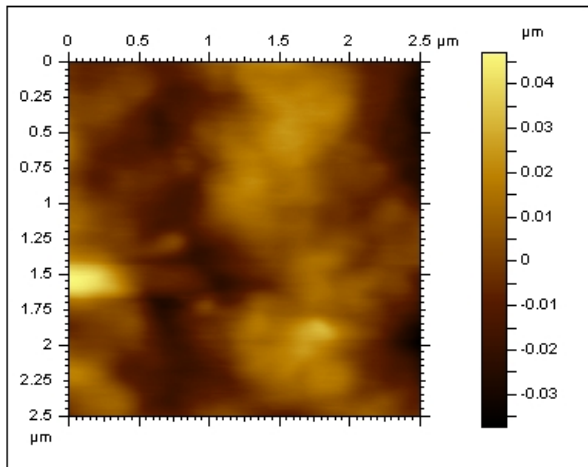


CS

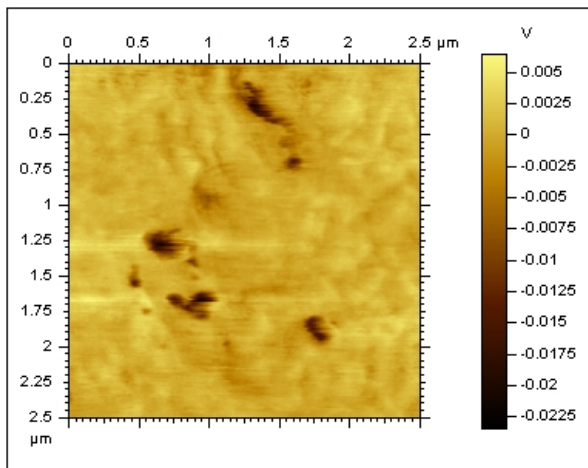
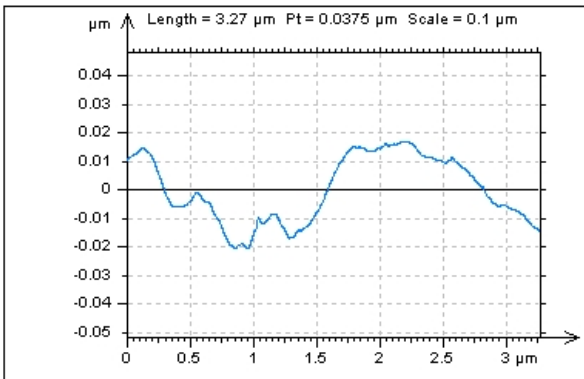




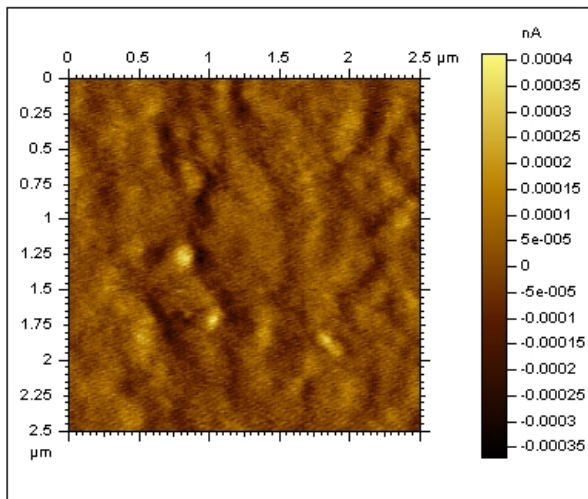
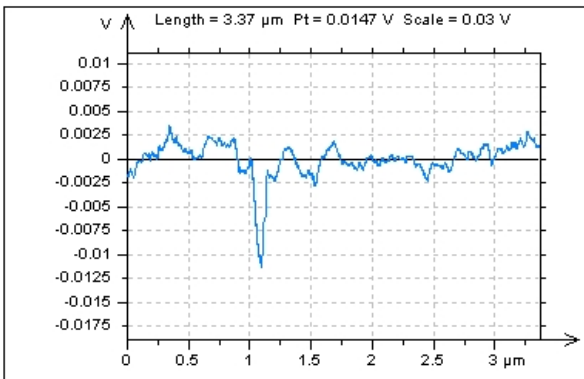
Appendix 2B



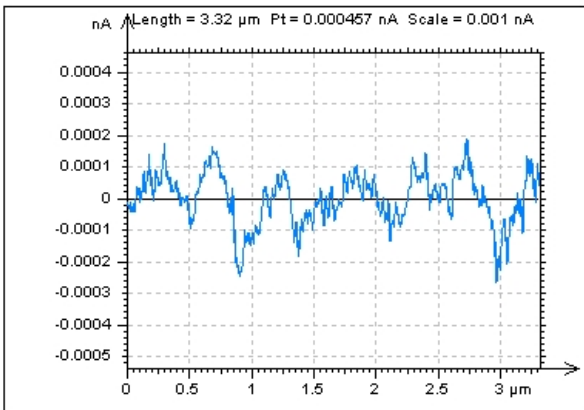
Sample bias 10 V
Topography

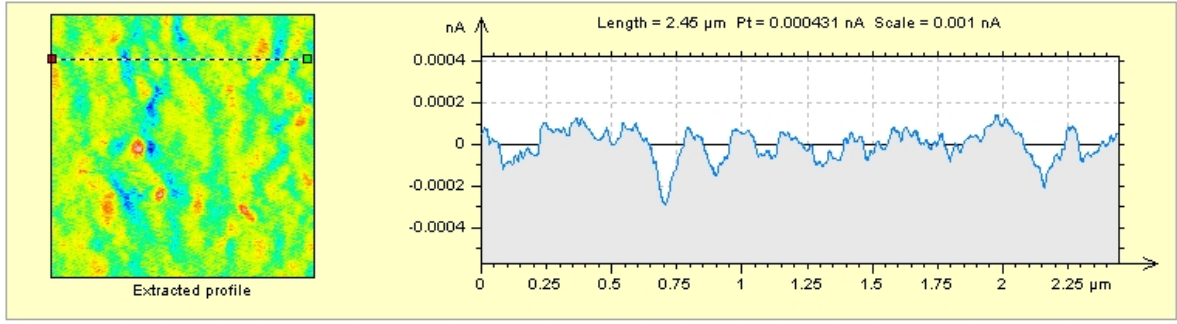
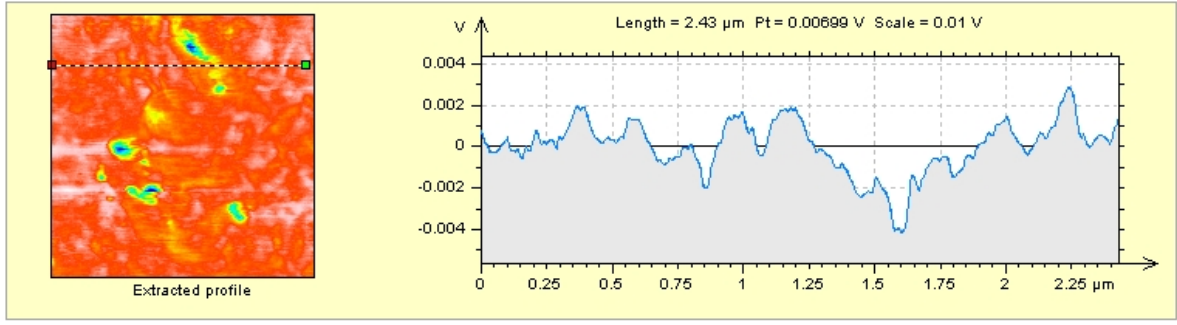
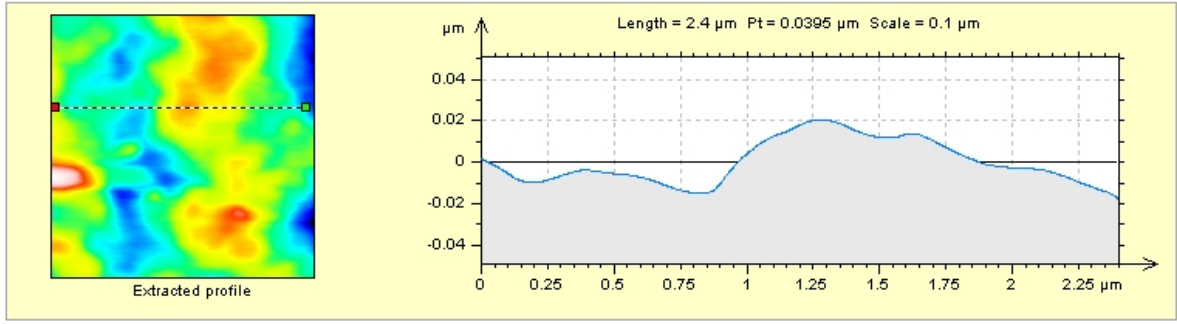
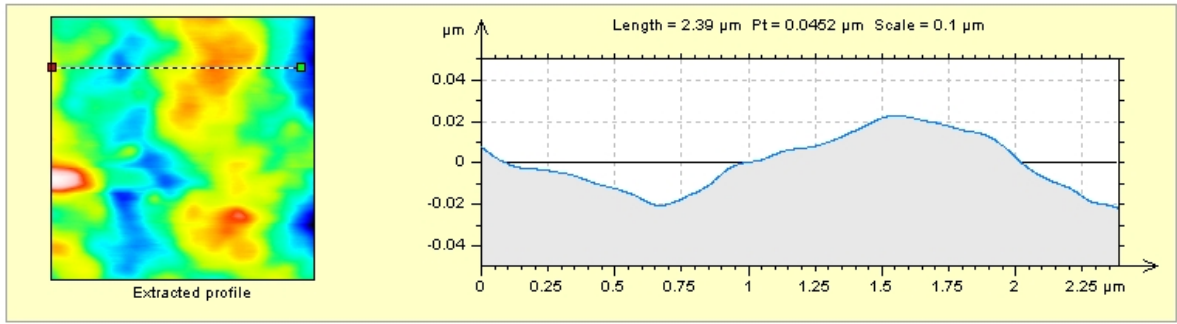


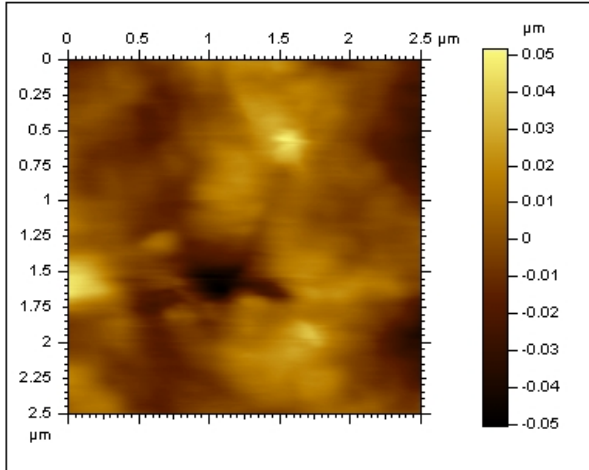
Friction



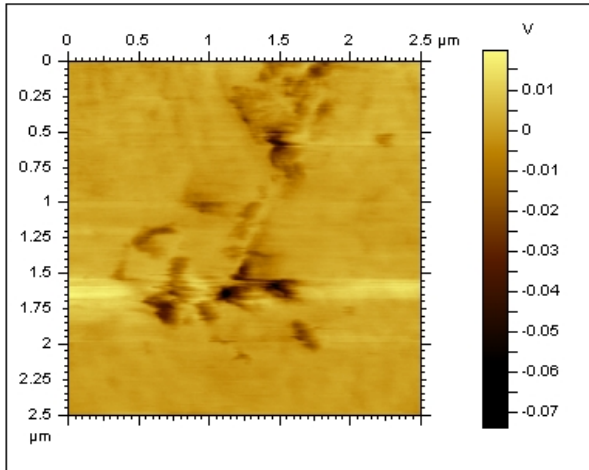
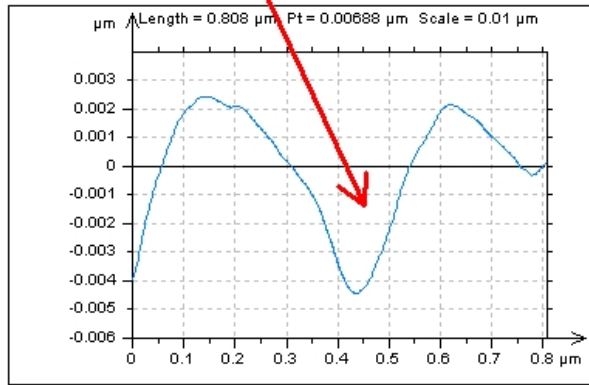
CS



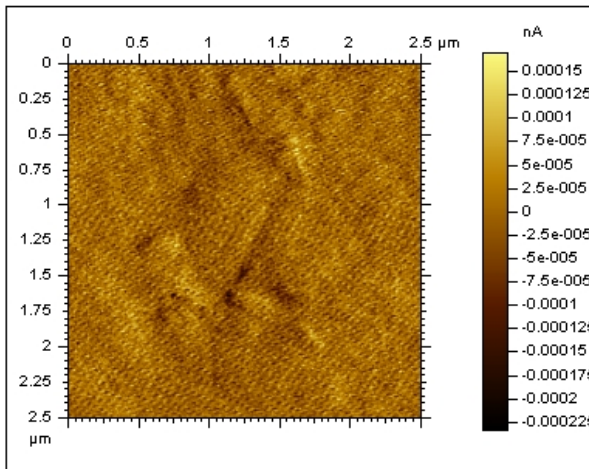
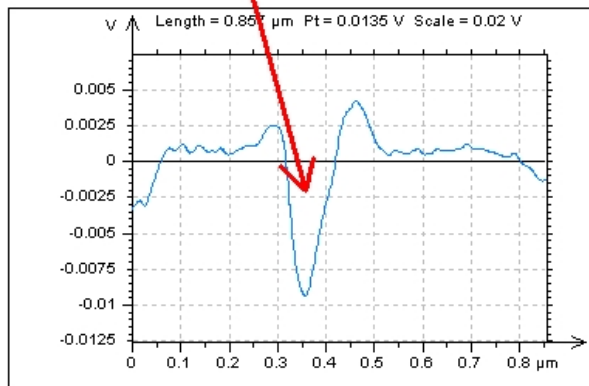




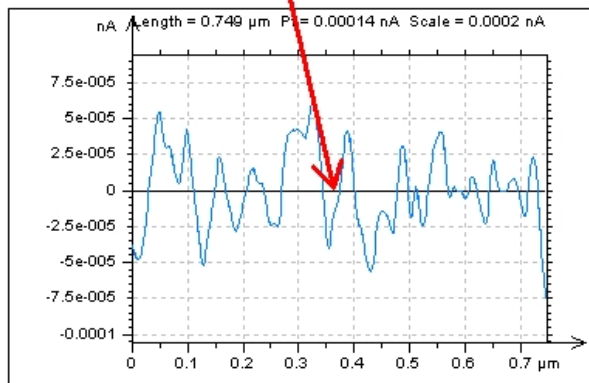
Scratch at 600 nN, Sample bias 10 V
Topography

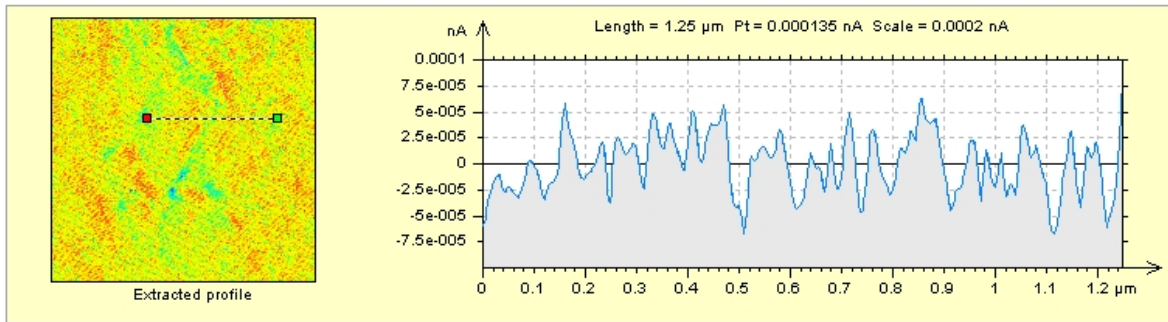
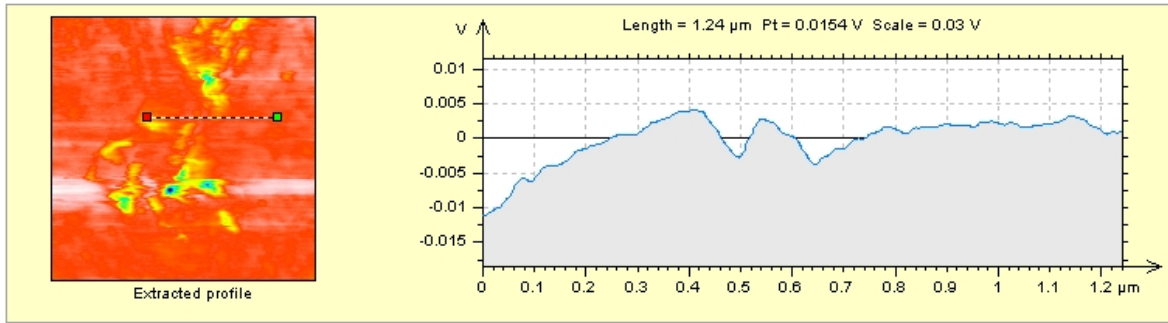
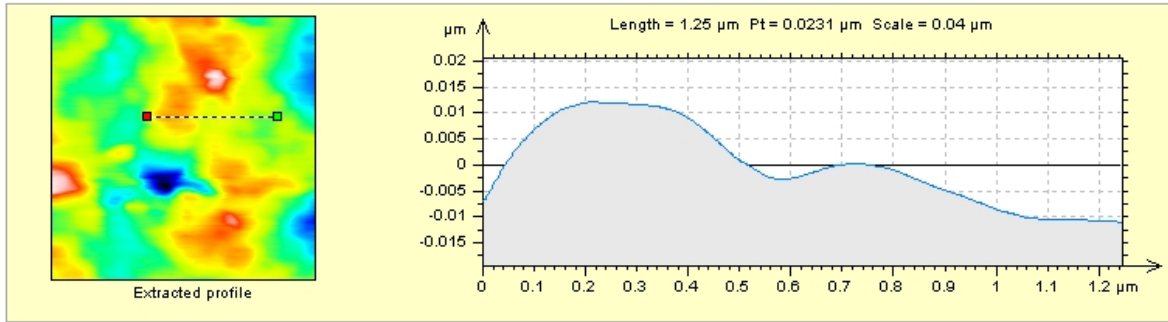
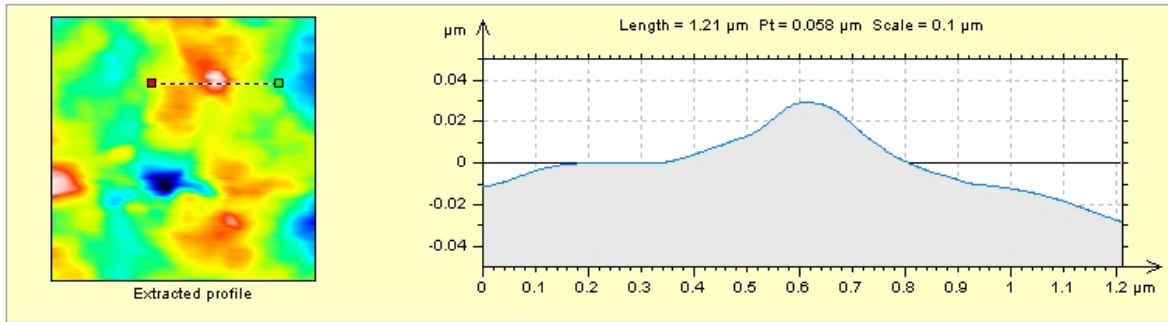


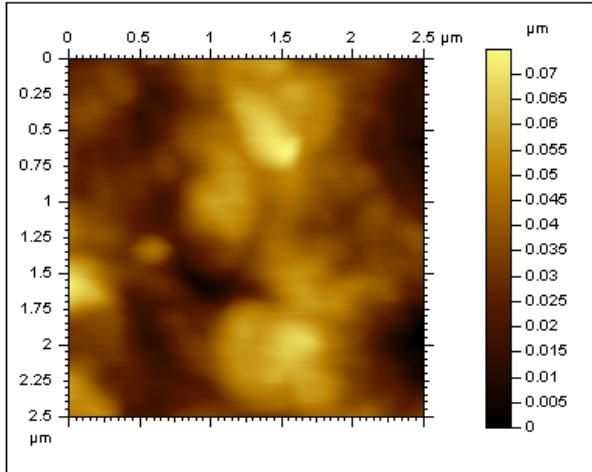
Friction



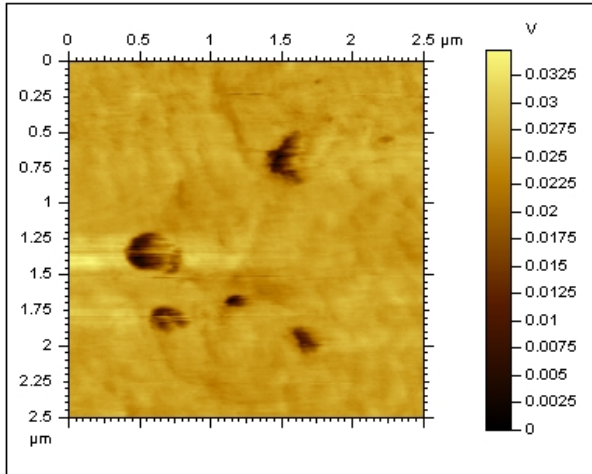
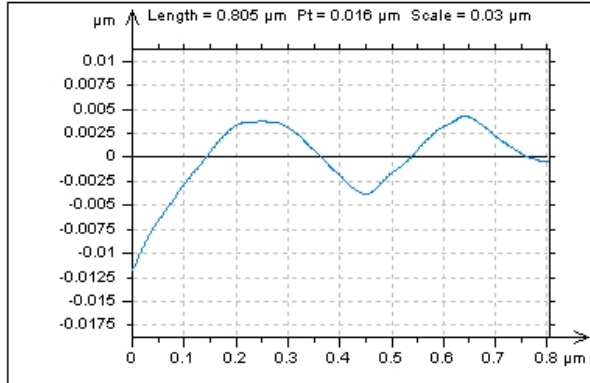
CS



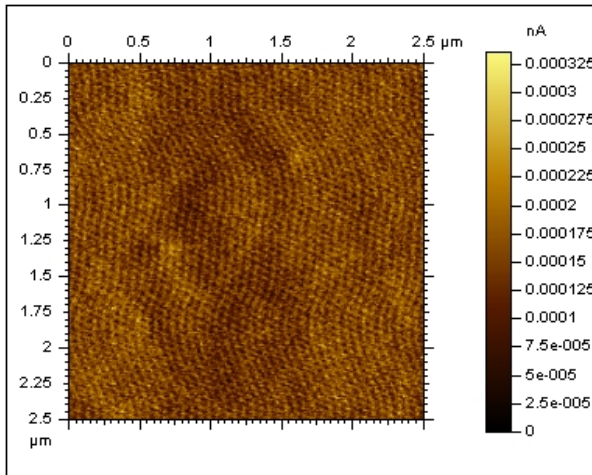
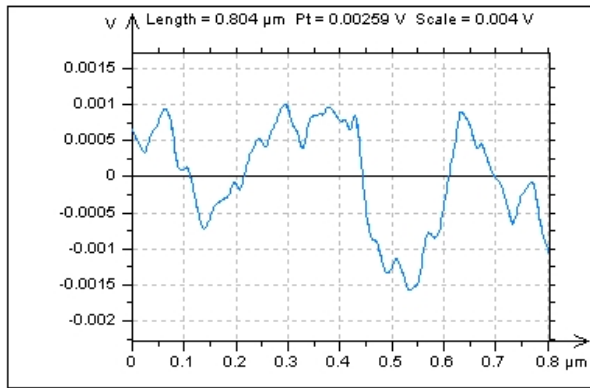




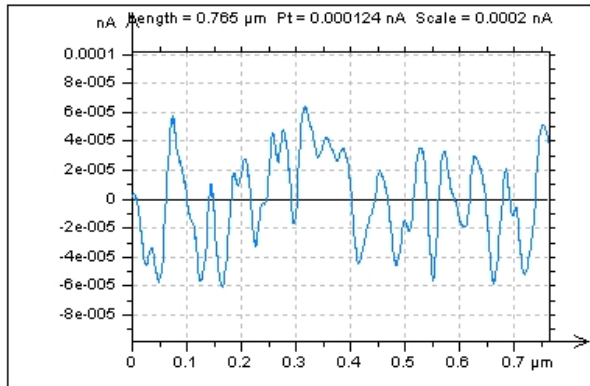
Scratch at 600 nN, Sample bias 10 V, after 4 scans
Topography

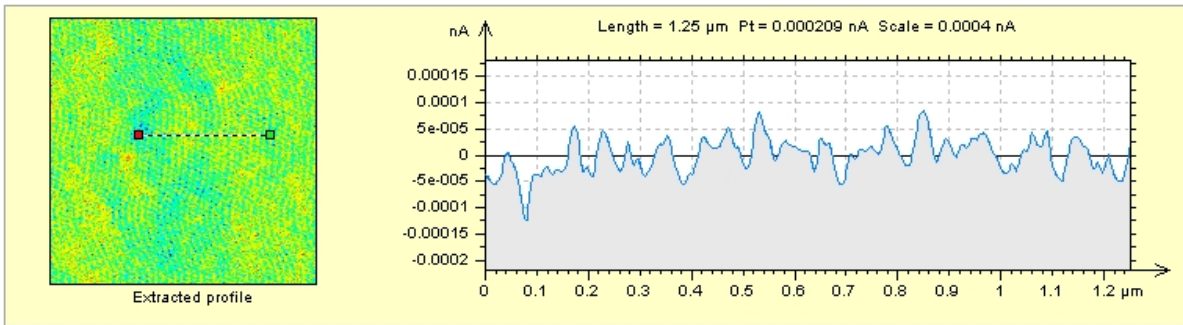
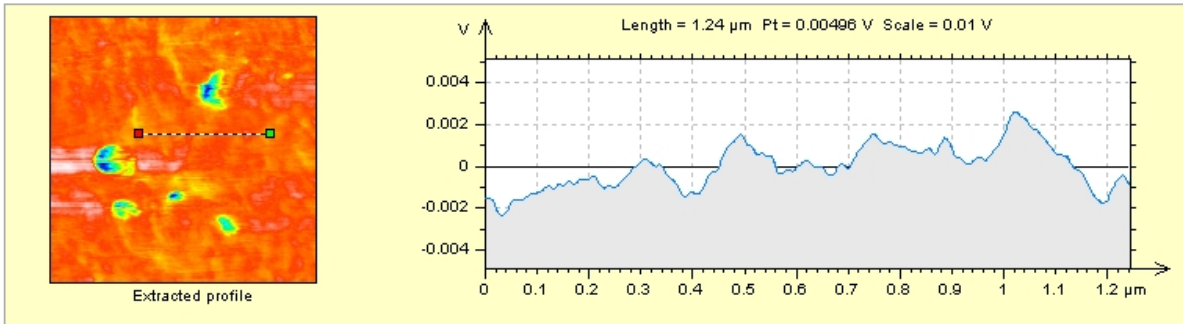
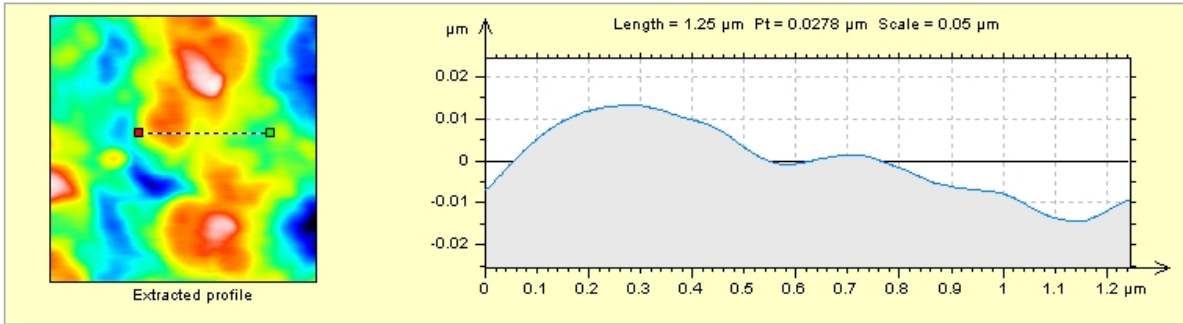
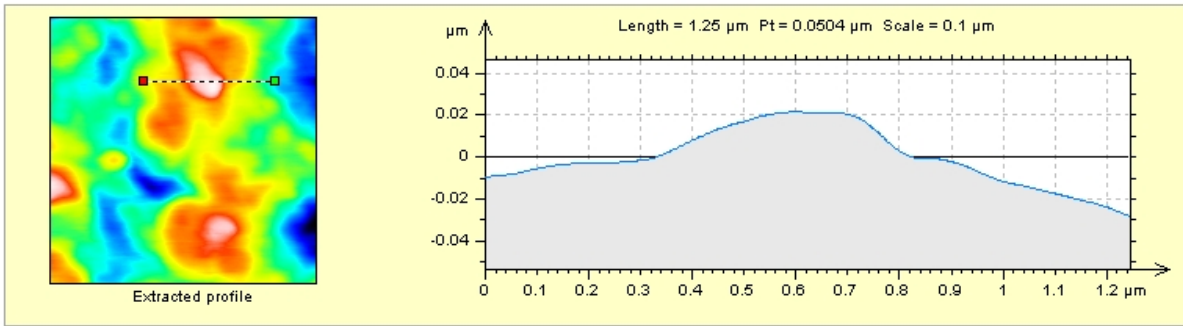


Friction

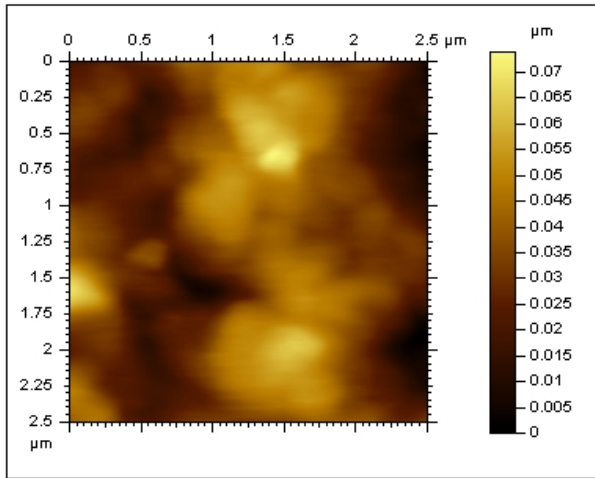


CS

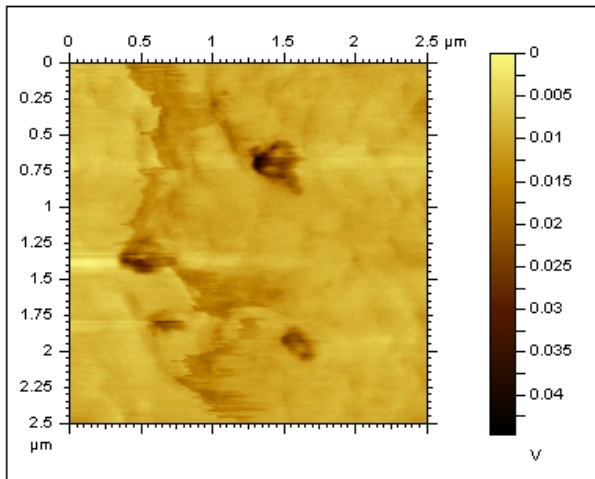
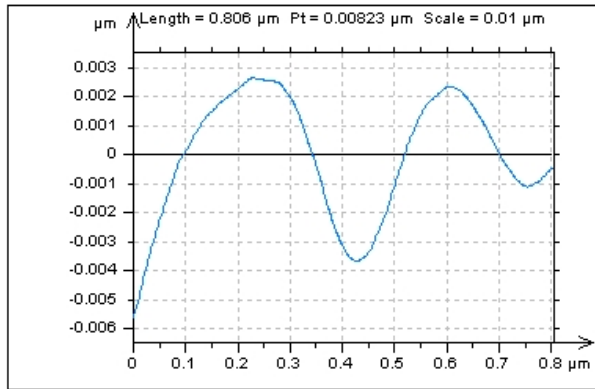




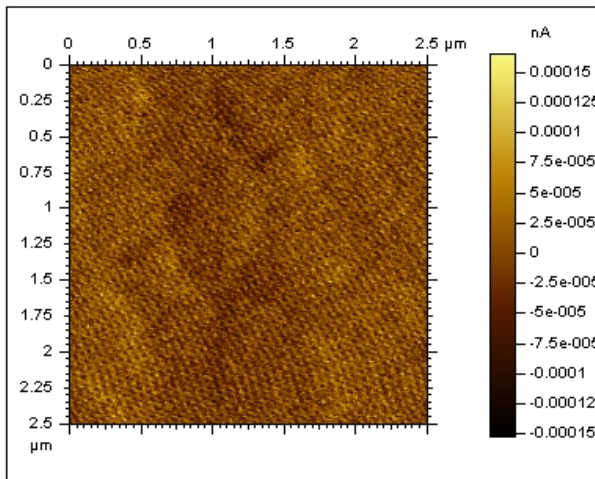
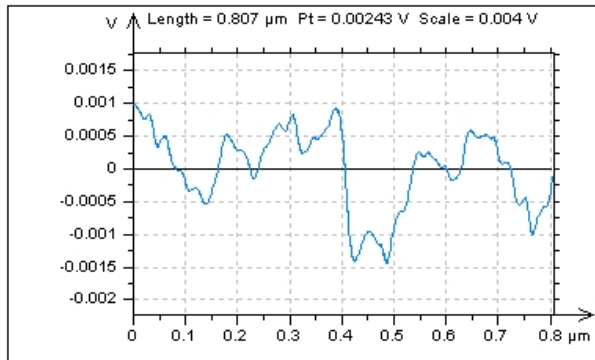
0



Scratch at 600 nN, Sample bias 10 V, after 8 scans
Topography



Friction



CS

