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Micro/nanotribological studies of materials using Atomic force microscopy

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by

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ABSTRACT

In this research study we focused on studying the tribological properties of materials using atomic force microscopy techniques (AFM). Especially the tribological properties of fiber materials like natural silks (spider and silkworm) and synthetic materials (Kevlar and Nylon) were studied at micro/nanoscales. It was found that the natural silks (spider silks, silkworm silks) exhibit lower coefficient of friction and work of adhesion values that the synthetic fibers (Kevlar, Nylon). While the natural silks exhibit comparable scratch resistance to the synthetic fibers at low loads, the synthetic fibers tend to exhibit significantly better scratch resistance at higher loads.

Durability of AFM tips were also studied by measuring the change in tip radius of the AFM tips and also utilized the atom probe tomographic (APT) techniques to examine the AFM tips. The measure of change in tip radius indicates the wear resistance of the tips. It was founded that coated tips (silicon nitride and DLC) has good wear resistance compared to pure Si tips and is also confirmed in APT studies.

CHAPTER 1. GENERAL INTRODUCTION

The overarching theme of this dissertation research work is to utilize Atomic force microscopy (AFM) to study the micro/nanoscale tribological properties of materials. This introductory chapter outlines the background, motivation and objectives of the research work.

1.1 Background

1.1.1 Nanotribology

Nanotribology is the study of friction/wear/lubrication at nano scales. The mechanisms of the interactions between two surfaces in relative motion , ranging from atomic to microscale , need to be understood in order to understand fundamental concepts of adhesion, friction, wear, indentation and lubrication process [1-12]. Nanotribology and nanoscale mechanics studies are necessary to understand the interfacial phenomenon in micro/nanostructures used in several applicaions. [3, 7-9, 13, 14].

Scanning probe microscopic techniques which include scanning tunneling microscope (STM), atomic force microscope (AFM) are widely used in micro/nanotribological studies.

1.1.2 Atomic force microscopy

Atomic force microscopy (AFM) is a very commonly used technique of microscopy which is a very high resolution type of scanning probe microscopy. The precursor to AFM was scanning tunneling microscope (STM) which was invented by Binning and his colleagues [15] and received Nobel Prize in Physics in 1986 for its invention. STMs can only be used to study the surfaces which are electrically conductive [16] and it operates by moving sharp tip close in close proximity with the surface of the sample. The tunneling current depends on the distance between the tip and the sample. The tip is rastered over the surface over a distance of 0.3-1nm, while the tunneling current is measured between them. It can be operated in two modes: constant current and constant height.

Based on their STM design, Binning el al. developed atomic force microscope (AFM) in 1986 [17]. AFM measures small forces between the tip and sample surfaces. By using AFM we can scan the surfaces of the samples which can be both conductive and non-conductive in dry, humid, vacuum and liquid conditions. AFM is operated by mounting a sample on a PZT tube scanner, which consists of separate electrodes which can used to precisely scan the surface of the sample in x-y plane in a raster pattern and can also move the sample in vertical z direction. A sharp AFM tip which is at the end of the cantilever is engaged or brought into contact with the surface of the sample and a set scan size would raster the tip over the surface of the sample. During the scanning the features and artifacts present on the surface of the sample cause the cantilever to deflect in vertical and lateral directions. A laser beam through a prism is directed onto the back of the cantilever. The laser beam is reflected of the back of the cantilever onto a photodiode detector (position sensitive detector) which is a split detector with for quadrants as shown in figure 1. The difference in signal of the top and bottom quadrants of the photodiode gives the vertical deflection signal of the cantilever.

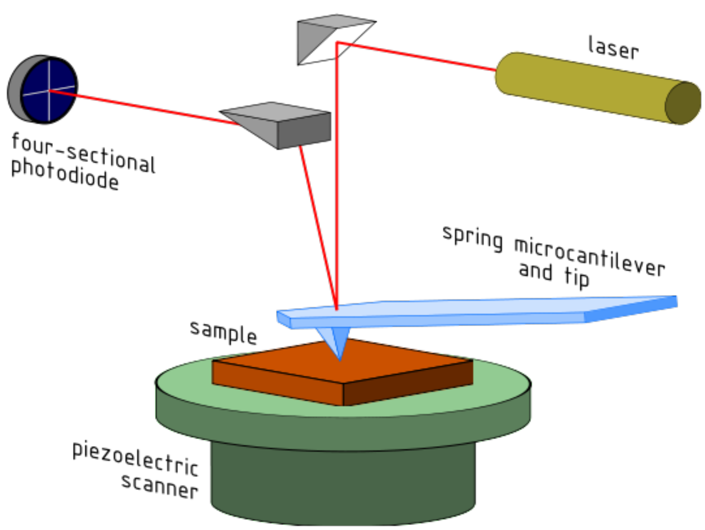

Fig 1. Principle of operation of AFM

(Source: http://en.wikipedia.org/wiki/File:AFM_schematic_(EN).svg)

Most commonly used types of modes in AFM are contact mode and intermittent-contact or tapping mode. Contact mode of operation is capable of obtaining very high resolution images. In this mode the deflection of the cantilever is kept constant known as set point. When the tip is continuously rastered over the surface of the sample, the features on the sample cause the cantilever to deflect and hence the change in the signal. This change in the signal is detected by the photodiode detector and the vertical deflection signal is measured by subtracting the signals

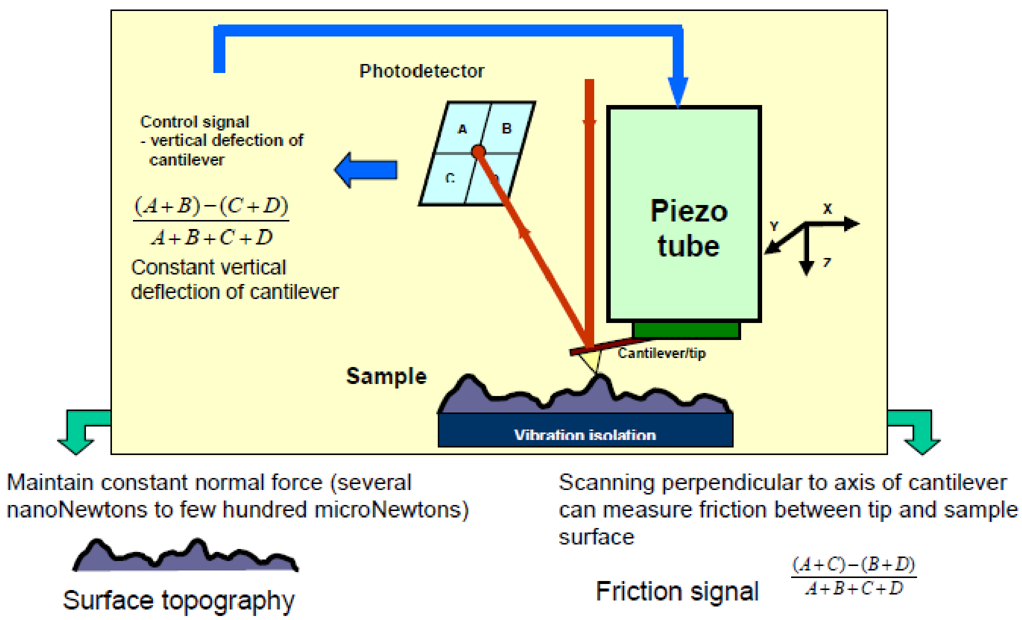

Fig 2. Contact mode operation of AFM

from top and bottom quadrants (A+B) – (C+D) as show in the figure 2. This signal is used in generating the topographical map of the surface..

The second common mode of operation is Intermittent contact mode or tapping mode. In this mode of operation the cantilever/tip assembly, with spring constant ranging from 20-100N/m is sinusoidally vibrated at its resonant frequency (50-400 kHz) by piezo mounted. This vibrating tip is then engaged onto the surface of the sample. During this process the amplitude will change and using the feedback control in the z-direction is adjusted to maintain a constant oscillating amplitude [18,19]. The feedback signal is used to track the surface of the sample. Generally tapping mode is used in topography measurements to minimize the effect of lateral forces and effects of friction. Using tapping mode we can use very sharp tips for scanning on surfaces without damaging. Especially very soft samples characterized using tapping mode.

AFM is a powerful tool to measure the tribological properties like roughness, friction, scratching/wear and nano indentation of the samples at micro/nano scales. Surface roughness measurements can be measured both by contact and tapping mode by scanning the area and measuring its RMS roughness value. To measure the coefficient of friction values the AFM tip was scanned at 90° scan angle on the surface of these fibers with a scan length and at a scan frequency. The friction response of the tip and sample was measured by taking the difference between forward and reverse scans of a scan line along the long axis of the cantilever. Coefficient of friction values are calibrated using method proposed by Ruan and Bhushan [17]. Adhesive forces are measured by using force-displacement curves in contact mode. Microscale scratching/wear measurements are taken using very hard tips.

1.1.3 Objectives

In recent years many researchers have expressed their interest in studying the properties of materials at micro/nanoscales. AFM techniques can be used in the fields of nanoscale sciences to analyze the materials to evaluate for its properties. My objective in this research work is to study the nanotribological properties of natural silk fibers and synthetic fibers and methods to evaluate near apex region of hard AFM tips using atomic force microscopy and atom probe tomography.

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CHAPTER 2. MICRO/NANOTRIBOLOGICAL PROPERTIES OF NATURAL AND SYNTHETIC FIBERS

Modified from a paper to be submitted to *Wear*

Srinath Kistampally[a], Nadia Fronning[b], Sriram Sundararajan[a,*]

Abstract

Several natural fibers such as spider silks exhibit superior mechanical properties which are derived from its bulk. In this study we focus on evaluating the microtribological properties of selected natural and synthetic fibers: dragline silk samples of Nephila Clavipes (a species of golden orb-web spider), silk worm silk samples obtained from white, cultivated Bombyx Mori silk (both natural and bleached type), Kevlar 6 fibers and Nylon 6 fibers. Interfacial parameters including work of adhesion, microscale coefficient of friction and wear resistance were evaluated using atomic force microscopy. We have observed that natural fibers have lower pull-off forces and lower coefficient of friction values compared to synthetic fibers. However synthetic fibers have greater wear resistance when compared to natural fibers.

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1. Introduction

In recent years there has been increased focus on studying mechanical properties of natural and synthetic silk fibers due to their applications in biomedical, defense and textile industries. Natural silk fibers are polymers made up of proteins that are spun into fibers by silkworms, spiders and other Lepidoptera larvae [1-5]. Spider silk (Nephila Clavipes and Araneus diadematus) and Bombyx Mori silkworm silk are the most common silks used today. These silk fibers are known for their biocompatibility, biodegradability and also for their exceptional mechanical properties like high tensile strength and toughness [5-8]. Romer and Scheibel [9] have studied the structure-function relationship of spider silk and have reported that spider silk consists of proteins which contains repetitive non-polar and hydrophobic amino acids which accounts for their exceptional mechanical properties. Genetic engineering including cloning is being used to construct spider silk proteins in bulk to overcome the limited commercial production of silk using spiders [4]. Bombyx Mori silkworm silk contains sericin and fibroin proteins with alternating hydrophilic and hydrophobic groups in the chain which are responsible for its exceptional mechanical properties [4, 10]. Hence both these silk fibers are used in making scaffolds for tissue engineering and for controlled released technology. The applications of silkworm silks and spider silks include sutures in biomedical industry, specialty ropes and fishing nets, ballistic applications, sports, textile industry [11]. When compared to spider silk, silkworm silk has low strength and low extensibility [6, 9] and under compression tests both these silks exhibit superiority over Kevlar [4]. Aramid fibers like Kevlar manufactured by Dupont are basically synthetic polymers have a remarkable combination of mechanical properties like high strength, resilience and light weight. Hence they are used mainly in defense industry. In the class of Nylons, Nylon 6 is the most characterized fiber due to its high tensile strength and elasticity especially at high temperatures, good resistance to abrasion and low coefficient of friction [12, 13]. Nylon 6 is hygroscopic in nature due the presence of H-bonds in its polymer chains [13]. Nylons are mainly used in textile industries and fishing industries. Porter et al [6] have reported that natural silks have high toughness and processing efficiency when compared to synthetic fibers like Kevlar and Nylon.

While many studies have investigated the mechanical properties of natural fibers and synthetic fibers relatively few studies have addressed the interfacial properties. Macro scale studies to evaluate tribological properties of Kevlar and its composites have been conducted [14, 15], but very little is known about their behavior at micro/nano scales. Mircro/nano scale tribological studies on natural materials like human hair have been studied elaborately by C. LaTorre and B. Bhushan [16]

Our main objective of this study is to evaluate the micro/nanotribological properties of selected natural and synthetic fibers. Specific properties that are reported include Microscale coefficient of friction, scratch resistance as well as other interfacial properties such as work of adhesion.

2. Experimental Methods

2.1 Materials

In this study we conducted experiments on dragline silk samples of Nephila Clavipes (a species of golden orb-web spider), Silk worm silk samples obtained from white, cultivated Bombyx Mori silk (both natural and bleached type) from Aurora silks and both Kevlar 49 fibers and Nylon 6 fibers from Goodfellow corporation. Figure 1 shows SEM images of various samples. Natural and bleached silkworm silk are fairly smooth on the surface compared to the spider silk. Spider silks typically have multiple strands attached to each other as shown in the figure. Both Kevlar and Nylon look fairly smooth on the surface and exhibit fibrous texture along its longitudinal axis.

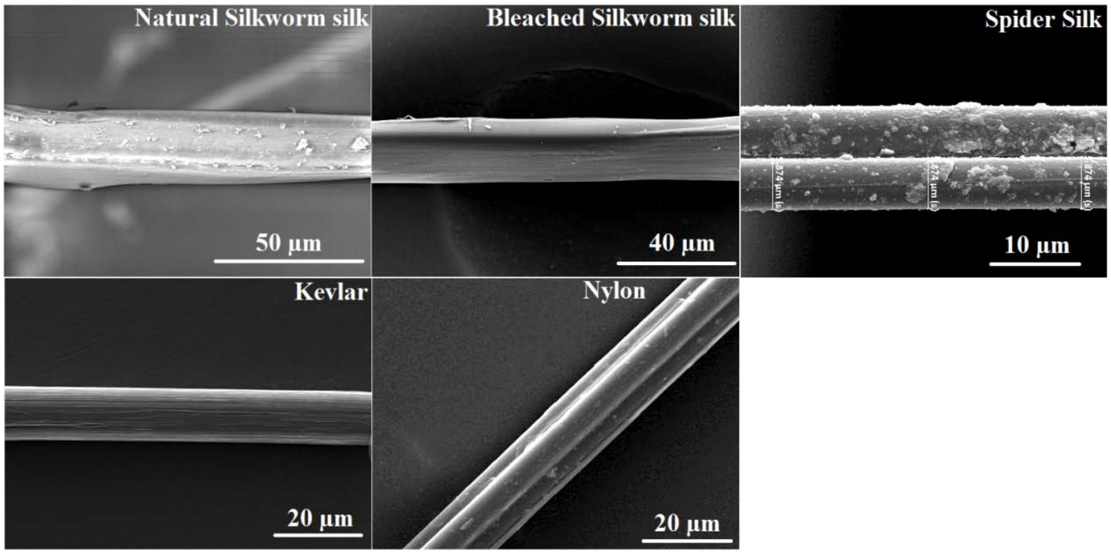

Figure 1 SEM images of (a) natural silkworm silk (b) bleached Silkworm silk, (c) spider silk and (d) Kevlar (e) Nylon

2.2 Atomic Force Microscopy

Samples were analyzed using atomic force microscopy (AFM). Contact mode atomic force microscopy (AFM) experiments were carried out with a Dimension^{TM} 3100 AFM (Nanoscope IV, Veeco Instruments, Santa Barbara, CA) at various humidity levels. Very thin samples of these fibers are carefully mounted by laying them on the carbon conductive tape which is a very good adhesive. This keeps the silk in place from rolling. All AFM measurements were conducted using rectangular silicon probes (CSC 37) from Mikromasch with tip radius ranging from 12-20 nm [17, 18]. The tip radii were characterized using a standard tip characterization sample (TGT 1) commercially available from Mikromasch. Spring constants of the cantilevers were calibrated using Sader's method [19] and ranged from 1.1 to 2 N/m. Surface topography was measured in contact mode over a scan size of 800nm x 800nm and roughness data was evaluated from these scans.

Pull-off forces on these fibers were measured by using force-displacement curves at different humidity conditions (8± 3% RH, 38± 3%RH and 60± 3% RH). The work of adhesion on these fibers was calculated from pull-off (adhesive) force data under dry conditions.

Friction measurements were taken at controlled dry conditions (8± 3% RH) to minimize the effects of adsorbed water vapor. To measure the coefficient of friction values the AFM tip was scanned at 90˚ scan angle on the surface of these fibers with a scan length of 2 µm and scan frequency of 1 Hz along the long axis of the fibers. The friction response of the tip and sample was measured by taking the difference between forward and reverse scans of a scan line along the long axis of the cantilever. Any small contribution towards the lateral deflection signal from non-frictional forces can be eliminated by using this method as described by Bhushan [20]. Coefficient of friction values are calibrated using the method proposed by Ruan and Bhushan [21]. The tip radius was characterized using a standard tip characterization sample (TGT 1) commercially available from Mikromasch.

The scratch resistance of the fibers was evaluated by performing reciprocatory scratches on the surfaces of the fibers at various loads (50, 100, 200 nN) using Si AFM probe. A stroke length of 2 µm in length at a sliding speed of 12 mm/s (scan rate of 3 Hz) was used. Each scratch test was conducted for reciprocatory 15 cycles corresponding to a total sliding distance of 60 mm. The scratches were evaluated post-test via a topography scan using the same tip.

3. Results and Discussion

Figure 2 compares the RMS roughness values for the various samples. Three roughness measurements were taken on each sample and the 90% uncertainty intervals are also reported. The roughness value of Nephila clavipes spider silk is highest among all the fibers whereas natural and bleached silkworm silks have the least roughness values.

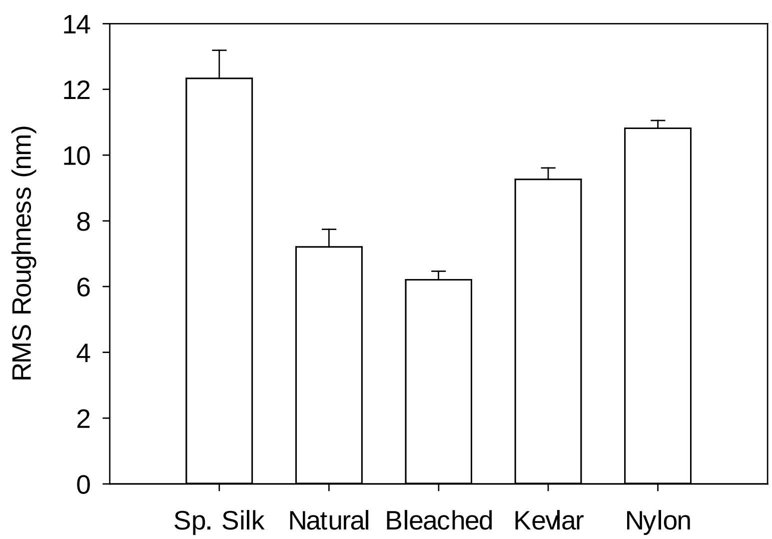

Figure 2 RMS roughness values of different fibers obtained from 800nm x 800nm scan size using AFM

Figure 3 shows the pull-off forces measured on the various samples as a function of relative humidity. Each reported values is an average of five measurements were taken at different regions on the surface of each sample. 90% uncertainty intervals are also reported. Overall, the natural silkworm silks exhibits the lowest pull-off forces, followed by the spider silks and the synthetic fibers. The variation in pull-off forces with increasing humidity can inform us of the hydrophobic or hydrophilic nature of the surfaces. Increasing humidity generally promotes increases water adsorption leading to increased contributions from capillary bridges between the tip and the surface towards the pull-off force. A hydrophobic material would exhibit less tendency to form adsorbed water and consequently less variation due to capillary forces as a function of increasing humidity. On the other hand, a hydrophilic surface would exhibit increasing contributions from capillary forces as a function of increasing humidity leading to increasing pull-off forces. The natural silkworm silk exhibit little variation in pull-off forces as the relative humidity increases. Studies have shown that the silk fibroin structure has repetitive hydrophilic and hydrophobic groups along the chain [10]. The pull-off force data indicate that the silkworm silks are essentially hydrophobic in nature. The surface of Nephila Clavipes spider silks also contain repeated alternate units of hydrophilic and hydrophobic regions [22, 23] and the overall behavior of surface appears to be hydrophobic in nature, as evidenced by the pull-off force data variation with humidity. Kevlar 49 fibers are known to be hydrophobic in nature [24] and hence shows a less variation in the pull of forces with increase in relative humidity when compared to Nylon which is hydrophilic in nature [13] and exhibits a very significant increase in pull-off force with increasing humidity. Based on the pull-off force data the silkworm silks appear to be the most hydrophobic in nature while Nylon 6 appears to be the most hydrophilic.

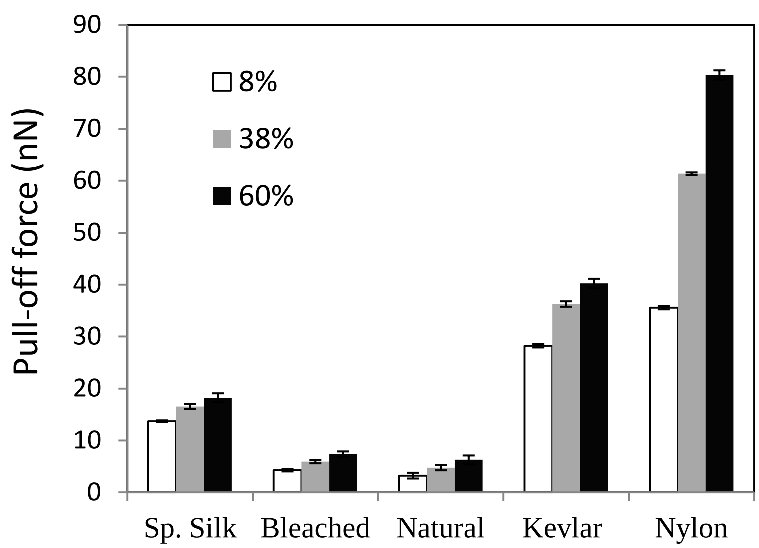

Figure 3 Pull-off forces of different fibers at different humidity conditions

The work of adhesion between the samples and a Si tip was estimated from pull-off force data at dry conditions and depends on appropriate contact mechanics model. During the pull-off force measurements no damage was observed on the surface of the samples and there was no significant change in the radius of the tip during the experiments. It is therefore reasonable to assume that the solid adhesion component is the dominant contributor to the pull-off force. The pull-off force (F_{po}) is related to the work of adhesion (W_{ad}) according to the following equation

$$F_{po} = -cRW_{ad} \qquad (1)$$

where R is the radius of the tip and c is a constant which depends on the contact mechanics model [25, 26] that best describes the contact condition.

The Johnson-Kendell-Roberts (JKR) model [27] is used when the surfaces in contact have large tip radii and exhibit strong adhesion forces while the Dejaguin-Muller-Toporov (DMT) model [28] is used when the surfaces in contact have weak adhesive forces and low tip radii.

The non-dimensional Tabor parameter (χ) is used to determine the appropriate contact mechanics model [29] and is given by equation (2).

$$\chi = \left(\frac{16R\gamma {W_{ad}}^2}{9K^2{z_0}^3}\right)^{1/3} \qquad (2)$$

where R is the radius of the tip, W_{ad} is the work of adhesion, z_0 is the equilibrium spacing of the two surfaces (taken to be 0.2 mm [30]) and K is the composite elastic modulus given by

$$K = \frac{4}{3}\left[\frac{1-\vartheta_1{}^2}{E_1} + \frac{1-\vartheta_2{}^2}{E_2}\right] \qquad (3)$$

where $\vartheta_{1,2}$ and $E_{1,2}$ are the Poisson's ratio and elastic modulus of the tip and sample respectively.

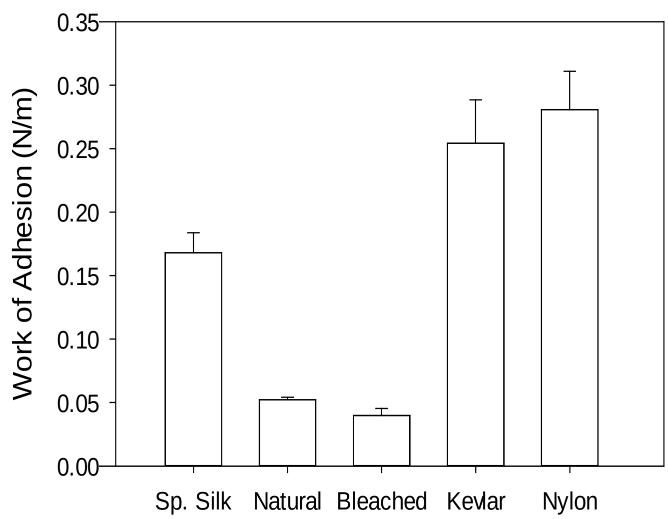

Figure 4 Work of adhesion of all fibers at dry condition

A Tabor parameter close to *zero* (χ < 0.0864) is indicative of the DMT model's suitability, while a value close to *one* is indicative of the JKR model's suitability [26]. The non-dimensional Tabor parameter χ was calculated on all the samples by initially assuming a certain model. In this case we initially assumed DMT model (where c = 2π) due to the small tip radius of the AFM tip. The resulting values of the Tabor parameter were all less than 0.06 for all the fibers suggesting that the DMT model was the appropriate one to use for our measurements. A check using the JKR model confirmed that it was not the suitable model, with Tabor parameter still yielding values close to 0.09. Consequently the DMT model was used to extract the work of adhesion.

Figure 4 shows the work of adhesion values of different fibers as calculated from the pull-off forces at 8% relative humidity and equation 1. The work of adhesion of synthetic fibers is generally larger than the work of adhesion of natural fibers. Silkworm silks have the lowest work of adhesion values compared to synthetic fibers.

Figure 5 shows the microscale coefficient of friction values of the fibers. Nylon has the maximum coefficient of friction compared to all other fibers. But we can also see that natural fibers have lower coefficient of friction values compared to the synthetic fibers.

The coefficient of friction values of the samples follow a trend that is very similar to the work of adhesion values. No significant wear was seen on the surface of the samples as a result of the friction measurements which suggests that the predominant friction was adhesive. Consequently, it is reasonable to expect the coefficient of friction of the samples to follow a similar trend with work of adhesion.

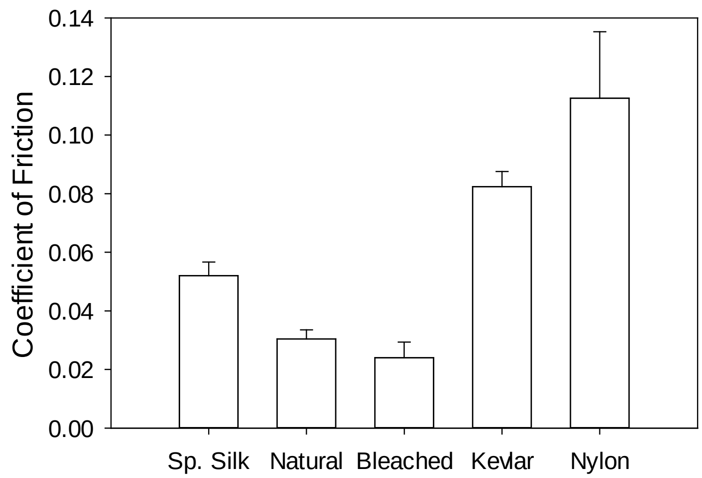

Figure 5 Microscale coefficient of friction of different fibers

The representative wear scans of spider silk, natural silkworm silk and nylon are shown in figure 6 and the average wear/scratch depth of the samples are shown in figure 7. Kevlar shows the highest scratch resistance followed by Nylon and natural silkworm silk which have comparable values. Spider silk shows very good scratch resistance upto 100nN, comparable to Nylon and natural silkworm. However it begins to exhibit poorer scratch resistance at 200nN. Bleached silkworm silks exhibit the poorest scratch resistance by a large margin compared to the other fibers.

From figure 6, the spider silks exhibit ploughing and wedge formation as the main mechanism of wear. The bleached silkworm silk shows some evidence of cutting debris on the sides of the tracks in addition to ploughing.

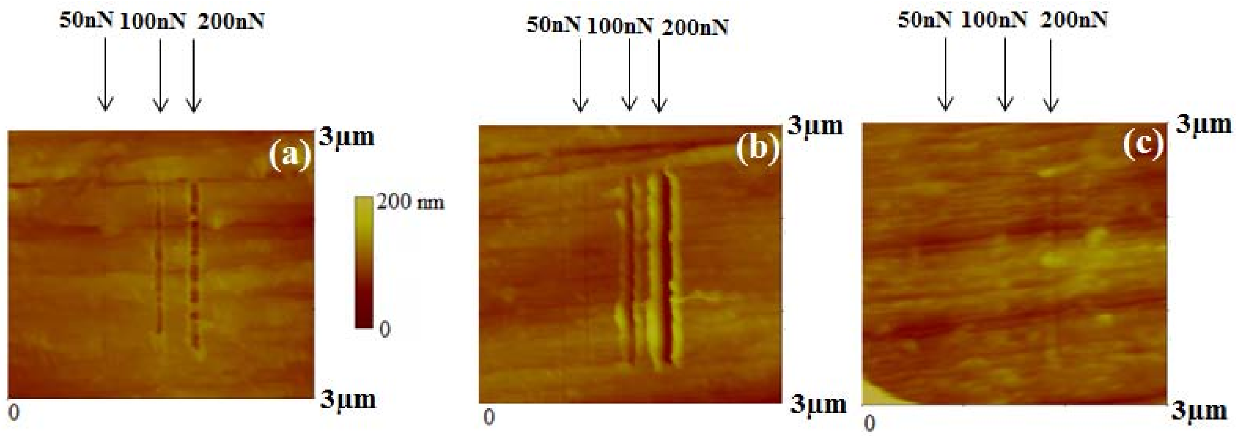

Figure 6 Representative wear scans of different fibers (a) Spider silk (b) Bleached SW silk (c) Nylon

The bleaching process and other degumming processes remove the Sericin which is present on the surface of the fibers [31] and may result in poor scratch resisistance.

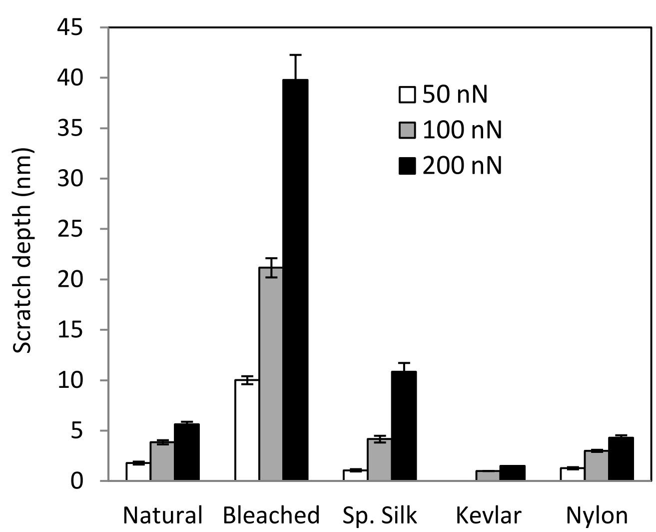

Figure 7 Scratch wear depth of different fibers

4. Conclusions

In this paper we studied the nanotribological properties of natural fibers and synthetic fibers. Table 1 summarizes the various surface micro/nanoscale tribological properties of the fiber samples measured in this study. Based on our studies, the natural silks (spider silks, silkworm silks) exhibit lower coefficient of friction and work of adhesion values that the synthetic fibers (Kevlar, Nylon). While the natural silks exhibit comparable scratch resistance to the synthetic fibers at low loads, the synthetic fibers tend to exhibit significantly better scratch resistance at higher loads. The bleaching process severely undermines the scratch resistance of the silkworm silk.

Table 1: Summary of surface and interfacial properties of selected natural and synthetic fibers. Average numbers along with 90% uncertainty intervals are reported.

Types of Fibers	Roughness [a] (nm)	Coefficient of Friction [b]	Work of Adhesion [c] (N/m)	Scratch depth [d] (nm)
Spider silk	12 ± 5	0.05 ± 0.02	0.17 ± 0.04	8 ± 5
Silkworm silk (Natural)	7 ± 4	0.03 ± 0.015	0.04 ± 0.01	4 ± 3
Silkworm silk (Bleached)	6 ± 3	0.025 ± 0.02	0.03 ± 0.02	25 ± 15
Kevlar 49	10 ± 4	0.085 ± 0.02	0.25 ± 0.08	2 ± 1
Nylon 6	11 ± 3	0.15 ± 0.5	0.28 ± 0.08	3 ± 2
Human hair [*]	10 ± 4	0.03 ± 0.01	---	---

[a] Roughness measured on a scan area of 800nm x 800nm
[b] Coefficient of friction measured using CSC 37 tip on a scan length of 2μm
[c] Work of adhesion measured using Si tip of radius 12nm on the surface of fibers at dry conditions
[d] Scratch depth measured by scratching a length of 2μm by applying a load of 100nN using Si tip
[*] Latorre, Bhushan; Structural, nanomechanical and nanotribological characterization of human hair (roughness measured on a scan area of 5μm x 5μm of a virgin Asian human hair)

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CHAPTER – 3

EVALUATING DURABILITY OF AFM TIPS

3.1 Introduction

Atomic force microscopy is a powerful tool for very high resolution characterization of the surfaces and in investigating nanoscale tribological properties of the materials [1]. The resolution of the AFM measurements critically depends on the geometry of the probe and is strongly affected by the degradation of the tip during scanning on the surface the samples. The durability of the AFM tips is considered to be one of the most important factor in carrying out the experiments on surfaces at nanoscales. To use a single probe numerous times and scanning it over a distance of several millimeters to kilometers (eg: Nanolithography) during its lifetime is one of the biggest challenge for the manufacturers.

Several techniques are used to measure the geometry of the tip which range from electron microscopy to using standard tip characterizer samples and algorithms to reconstruct the images obtained [2-4]. To study the chemical composition and material structure of near apex region of the tip is an arduous task. Three dimensional atom probe tomography has been used successfully to study the material composition and structure of the near apex region of the AFM tips. In this research work, we studied the durability of few hard AFM tips by measuring the change in tip radii after rubbing it against the hard sapphire.

3.2 Materials and Methods

AFM tips (uncoated NSC 15 Si tips, NSC 15 LS and NSC15 Si_3N_4 and DCP 20 tips) are used to study their durability. Uncoated NSC 15 Si tips (Mikromasch) have a conical tip shape and n-type doped with phosphorus with spring constant in the range of 35-45 N/m, NSC 15 LS and NSC 15 Si_3N_4 (Mikromasch) are both CVD coated with different thicknesses of Si_3N_4 coatings which results in tip radii of 30 and 20 nm respectively, DCP 20 (NT-MDT, K-TEK nanotechnology) is a boron doped Si tip coated with diamond like carbon (DLC) with a nominal tip radius of 30-45nm and spring constant of 65-90 N/m.

The durability of tips was studied by measuring the change in contact pressures(stresses) at the interface by rubbing it against the hard sapphire for 5 min at a load of 100nN on a scan area of 5µm x 5 µm at a scan rate of 1 Hz. The initial tip radius of the each tip was measured by using a standard TGT 1 tip characterizerInitial tip radius of NCS15 Si tip is 15 nm, NCS15 LS is 25nm and NCS15 Si_3N_4 is 16nm and DCP tip is 28nm. . Now each tip is rubbed against hard sapphire sample and change in the tip radius was measured. By using these changes in the tip radius we can measure the changes in the interfacial pressures which is a measure of durability.

Figure1 below shows change in the pressures and percentage change in the contact pressures acting on the tips at the interface. A load of 100nN load is applied and rubbed against sapphire for 5 min for three times. After the end of three runs the changes in pressures of pure Si NSC 15, NSC 15 LS and DCP 20 tips is found to be almost similar. And the percentage change in pressures is also similar as shown below.

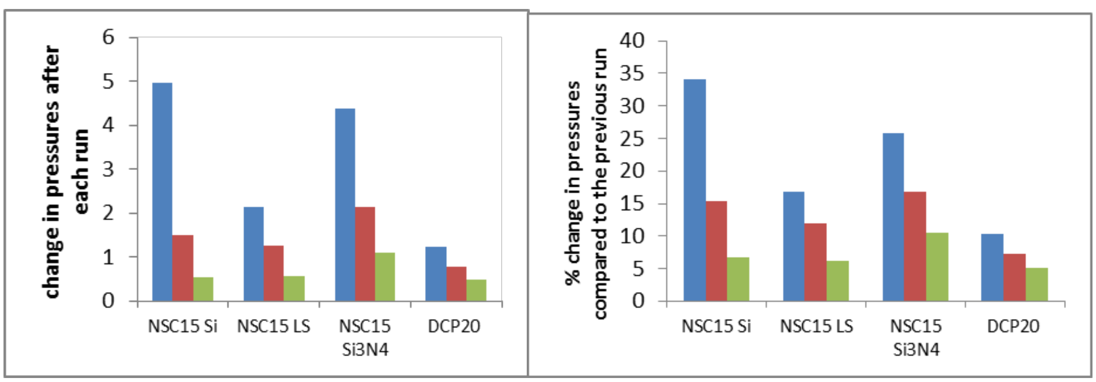

Figure 1. Change and percentage change in average pressures of AFM tips after rubbing against sapphire

These tips were also examined using atom probe tomography. APT techniques are now capable of determining the three dimensional structures and chemistry of AFM tips [5]. AFM tips possess necessary geometry which makes them suitable for APT analysis. The tips were analyzed as received using a commercially available atom probe microscope (LEAP 3000X Si, Cameca Instruments Inc.) in the pulsed laser mode.

Table1. Parameters for APT analysis of the various SPM tips. All samples were run in pulsed laser mode at 200 kHz and 0.5% evaporation rate.

(Source: C.J. Tourek's Ph.D Thesis)

Tip Type	Material	Sample Temperature (K)	Laser Power (nJ)
NSC15	Si(100)	50	0.3
NSC15 Si_3N_4	Si3N4 on Si(100)	50	0.9
NSC15 LS	Si3N4 on Si(100)	100	1.2
DCP20	DLC on Si(100)	125	1.3

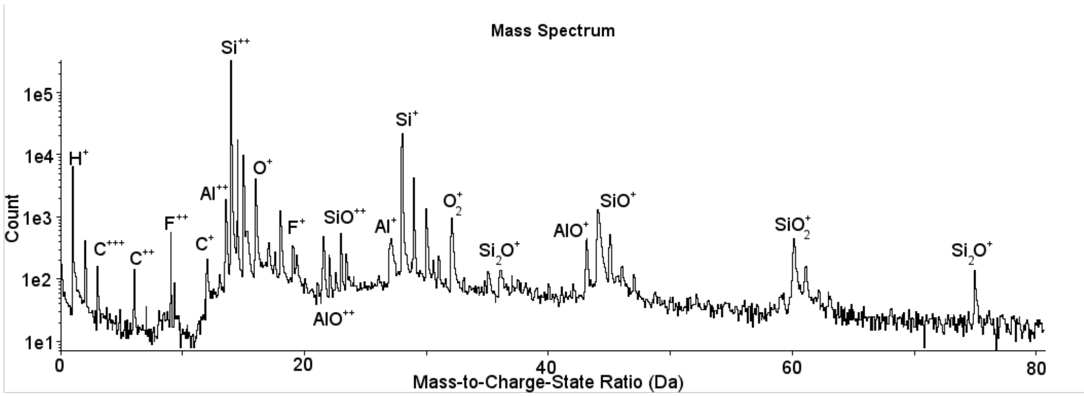

Figure 2 Mass spectrum from APT analysis of NSC 15 Si tip

Figure 2 shows the mass spectrum of NSC 15 Si tip. Silicon ions and the native oxide of Silicon (Si^+, Si^{++}, and Si_2^+, O^+, O_2^+, SiO^{++}, SiO^+, SiO_2^+, Si_2O^{++}, and Si_2O^+) are seen in the spectrum along with Al^+, Al^{++}, AlO^+ and AlO^{++}, C^+, C^{++}, C^{+++}, F^+ and F^{++}.

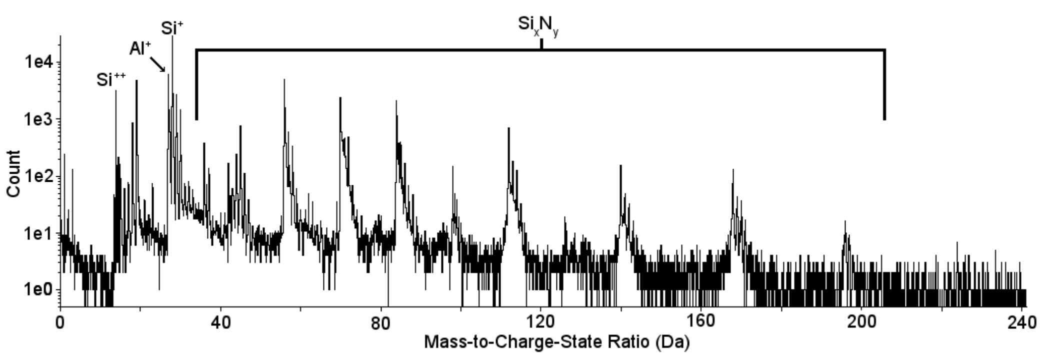

Figure 3 Mass spectrum from APT analysis of Silicon nitride coated NSC 15 tips

Figure 3 shows the mass spectrum from APT analysis of NSC 15 Silicon tips coated with silicon nitride. The thicknesses of these coatings vary for NSC15 LS and NCS15 Si_3N_4. Silicon nitride is used as hard coating to minimize the wear of the tips during the nanotribological studies. The mass spectrum shows Si peaks along with multiple peaks of silicon nitride compounds. High laser power was necessary in the case these coated tips to field evaporate compared to uncoated silicon tips. Since Si and N have mass to charge ratios that are multiples of each other 28 and 14 respectively, makes it difficult to distinguish the compounds of higher mass compounds.

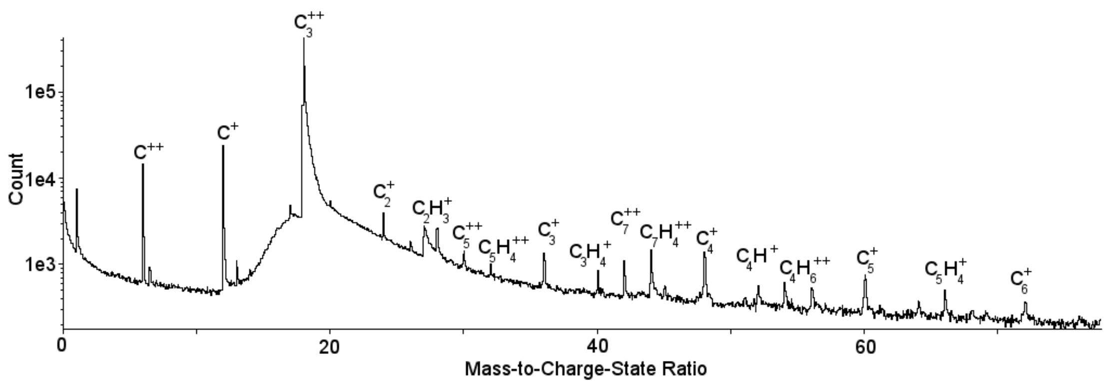

Figure 4 Mass spectrum of DLC coated AFM tip (DCP 20)

Figure 4 shows the mass spectrum of AFP tip coated with diamond like carbon (DLC). DLC coatings have very good wear resistance and used extensively in nanoscale wear and nanoindentation studies.

These tips required high laser power and temperature to field evaporate the ions. These coatings typically contains C_3^{++} in majority and also C_2^{+}, C_3^{+}, C_3^{++}, C_4^{+} C_4^{++}, C_5^{+}, C_6^{+}, C_7^{+} in minor quantities as shown in the mass spectrum.

3.3 Conclusions

The near apex regions of several AFM tips were successfully analyzed using atomic force microscopy and atom probe tomography. In the AFM studies the change in the contact pressures of NSC15 Si_3N_4 probe is highest compared to all other tips. Pure Si NSC 15, NSC 15 LS and DCP 20 tips show almost similar trend in change in the contact pressures. In the APT studies uncoated Si tips needed much less temperature and laser energy to field evaporate compared to the tips coated with silicon nitride and diamond like carbon. In the case of the coated tips, field evaporation during the atom probe runs stopped when the interface was reached. APT runs on uncoated tips (NSC15) and tips coated with silicon nitride (NSC15 LS and NSC15 Si_3N_4) are successful more often compared to diamond like carbon (DLC) coating DCP tips. Hence, we can use AFM and APT studies to quantify the contamination of tips and analyze the material transfer during wear and scratch tests.

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CHAPTER-4

CONCLUSIONS

Atomic force microscopy was used to study the nanotribological properties of natural fibers and synthetic fibers. Various surface micro/nanoscale tribological properties of the fiber samples measured in this study. Based on our studies, the natural silks (spider silks, silkworm silks) exhibit lower coefficient of friction and work of adhesion values that the synthetic fibers (Kevlar, Nylon). While the natural silks exhibit comparable scratch resistance to the synthetic fibers at low loads, the synthetic fibers tend to exhibit significantly better scratch resistance at higher loads. The bleaching process severely undermines the scratch resistance of the silkworm silk.

We have also studied the durability of AFM tips by measuring the change in tip radius after rubbing it against the hard sapphire sample. In the AFM studies the change in tip radius of NSC15 Si probe is highest compared to all other tips. NSC 15 LS and NSC15 Si_3N_4 tips show almost similar trend in change in the tip radius. Change in tip radius of the DLC coated DCP tips is very less compared to all other tips. We have also successfully examined the near apex regions of several commercially available AFM tips using atom probe tomography. Conical Si tips coated with silicon nitride and DLC were successfully analyzed in pulsed laser mode. The coated AFM tips required high temperatures and laser energies to field evaporate compared to uncoated Si tips.

Future Study

We can implement the same AFM techniques to evaluate the nanotribological properties of other fibrous materials and biomaterials. The nano scale hardness of these fibers can be studied using nanoindentation techniques. The transferred material on the near apex region of the AFM tips can be studied at nano scale using APT. The wear on hard materials in fluids could be studied using AFM tips and in turn can be analyzed by APT.