

A Study of Moisture Damage in Plastomeric Polymer Modified Asphalt Binder Using Functionalized AFM Tips

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ABSTRACT

In this study, moisture damage in plastomeric polymer modified asphalt binder is investigated using Atomic Force Microscopy (AFM) with chemically functionalized AFM tips. Four different percentages of plastomeric polymers and two antistripping agents such as Kling Beta and Lime are used to modify a base asphalt binder. Chemical functional groups such as $-\text{COOH}$, $-\text{CH}_3$, $-\text{NH}_3$, and $-\text{OH}$, that are commonly present in plastomeric polymer modified asphalt system, are used to functionalize the AFM tips. The force distance mode of AFM is used to measure the adhesion forces between a modified asphalt sample surface and the functionalized AFM tips. This enables the measurement of adhesion within an asphalt binder system. It is shown that the adhesion force values in dry sample changed substantially from that in wet conditioned samples. It is evident from this study that plastomeric modification does not help reduce moisture damage in asphalt. The percentage change in adhesion forces due to moisture is about 20 nN for the lime modified samples, and about 50 nN for the Kling Beta modified samples. This indicates that lime is more effective than Kling Beta for reducing moisture damage in plastomeric polymer modified asphalt.

Keywords: Atomic Force Microscopy, Adhesion Force, Asphalt, Moisture Damage, Antistripping Agents, Plastomer and Surface Roughness.

1. INTRODUCTION

Quantifying adhesion force of asphalt binder is an important issue for understanding moisture damage behavior of asphalt concrete. So far, adhesion force between asphalt and aggregate has been determined largely at macro-level involving asphalt concrete samples. The macro-level adhesion lacks in explaining moisture damage that occurs within an asphalt binder system. Very recently some research have done adhesion test on asphalt film using Atomic Force Microscopy (AFM). However their study was limited to only silicon tip [1]. The present study uses functionalized tips and advanced software (non-contact and contact mode) to capture image and adhesion in asphalt samples. The work presented in this paper focuses on capturing the microscopic image of asphalt film and measurement of roughness of film surface using an AFM and on determining the moisture damage in plastomeric polymer modified asphalt using the AFM functionalized tips.

2. BACKGROUND

Moisture damage within the binder and/or at asphalt-aggregate interfaces has been studied by several researchers [2, 3, 4, and 5]. Recently, surface free energy of asphalt and aggregate has been empirically related to the moisture-induced damage of asphalt concrete [3, 6]. Surface free energy of asphalt and aggregate is indirectly measured using the Wilhelmy plate, sorption device, and Youn-Dupré equation. However, the Wilhelmy plate method cannot differentiate between the functional groups. For example, the surface free method fails to differentiate between actions of carboxylic acid (bad) and carbonyls (good), or carboxylic acid (bad) and nitrogen compound (good) under wet condition. Also, the Wilhelmy plate technique cannot clearly distinguish between untreated asphalt and asphalt treated with amine antistrip. By the same token, the universal sorption device requires vacuum degas preconditioning, which is very different from the mixing plant conditions [6]. Very recently, a study has attempted to measure surface force of asphalt cast onto glass slide substrates using AFM [7]. Their study was limited to asphalt morphology and did not include functionalized tips. The present study has included functionalized tips to measure intermolecular forces (i.e., adhesion/cohesion) in polymer modified asphalt systems.

Though various macro-micro scale tests and models of moisture damage of HMA have been suggested, the fact is that these test and models cannot explain why moisture damage occurs in HMA mixtures. As moisture related damage initiates from the atomic and molecular level, it is hypothesized in this study that a nano and micro level testing is necessary element in estimating the moisture damage problem. However, most of these tests did not develop an understanding of the bond damage phenomena, and so as a result moisture damage is still one of the most common and complex unsolved problems. Hence, the need for a fundamental approach, which would elucidate and quantify bond strength in asphalt concrete, is evident [5, 8].

Usually two different types of additives or antistripping agents have been using to control moisture damage in the area of asphalt pavement engineering. They are chemical (liquid) and lime (non-liquid) types (Hicks 1991). The chemical or liquid types promote some uniform type of wetting of the aggregates hence reduce the surface tension of the asphalt binder. A study [10] found that moisture damage of asphalt concrete pavements is a problem experienced by more than one-half of the State Highway Agencies (SHA) in the United States. In a seminar [11], it is reported that 82 percent of highway agencies require

the use of an antistripping agents in hot mix asphalt concrete or HMA.

In the pavement community, one group of researchers believes that antistripping agents are helpful to reduce moisture damage or stripping. As a result, most of agency uses 0.5 to 1.0% antistripping. However the fact is moisture damage or stripping is still a prevalent problem of our pavements. As a result, a group of researchers believe that antistripping agents do not help reduce moisture damage at all. So far, macro-scale strength test (e.g. AASHTO T 283) has failed to resolve this conflict. Often time, a mixture with or without antistripping agents has shown failure in the field. In addition, laboratory macro-scale testing has shown false negative or positive with or without antistripping agents. The reason for this is that antistripping agent is very small (0.5 to 1.0%) in binder, which is even very small (5 to 6%) compared to the aggregate or total mix. Some believe that chemical antistripping agents evaporate or leave the binder surface during mixing and compaction, which requires to be done at a very high temperature (160°C). No test procedure has been developed on binder to see whether antistripping agents work or not. There are State DOTs that rely on lime than chemical antistripping. For example, New Mexico DOT uses 1.0% lime in asphalt binder for all mixes. However, some contractors have shown interest in using morlife in New Mexico. Therefore, there is a need for studying whether antistripping agents have any effect on adhesion loss. If so, then what percentages is the most effective. Also, it is important to know which type of antistripping is most effective. Similarly, it will be interesting to know whether lime is more effective than chemical antistripping agents. All of these are done in this study based on AFM measured adhesion force or also known as pull-off force.

A laboratory experiment was performed to investigate the effectiveness of cementitious fillers on moisture susceptibility of HMA mixtures [12]. They utilized five types of cementitious fillers namely, fly ash, cement kiln dust, and three types of hydrated lime with different finenesses. The laboratory performance of HMA mixtures subjected to moisture conditioning was evaluated through the following tests: dynamic modulus test; superpave indirect tensile tests; and tensile strength ratio test. The test results indicate that the cementitious fillers were generally effective in reducing the moisture susceptibility of HMA mixtures. The finer the hydrated lime particle, the more resistant the asphalt mixtures. In addition, dynamic shear rheometer test was conducted on asphalt mastics to explore the stiffening effect of different cementitious fillers.

3. PERFORMANCE OF LIME MODIFIED ASPHALT CONCRETE

Research was performed to evaluate field samples and pavement performance data from untreated and lime treated pavements [13]. The properties of untreated and lime-treated mixtures from field projects in the southern and north-western parts of Nevada indicated that lime treatment of Nevada's aggregates significantly improves the moisture sensitivity of HMA mixtures. The study showed that lime treated HMA mixtures become significantly more resistant to multiple freeze-thaws than the untreated mixtures. The long term pavement performance data indicated that under similar environmental and traffic conditions, the lime-treated mixtures provided better performing pavements with fewer requirements for maintenance and rehabilitation activities. The analysis of the impact of lime on pavement life indicated that lime treatment extends the

performance life of HMA pavements by an average of 3 years. This represents an average increase of 38% in the expected pavement life. A study on the effects of conditioning the mixes for longer durations was performed [14]. Their report addresses two issues, by preparing and testing mixtures made with fresh binder for indirect tensile strength after conditioning the samples for 1, 7, 28, 90 and 180 days, and samples prepared from binder stored for 3 days at 163°C after conditioning them for 1, 28 and 90 days. The results of this study indicated that hydrated lime and the liquid anti-stripping agents were equally effective for the mixes used in this research when conditioned beyond 1 day. In the case of samples prepared from stored binder, there was no significant difference in the effectiveness of hydrated lime and the liquid anti-stripping agents even after conditioning for 1 day. Though it was observed that none of the ASA treatments performed better than others in the case of samples prepared with stored binder, it was also observed that almost all mixes gave significantly similar wet ITS and TSR values as samples prepared from fresh binder.

4. EFFECTIVE PERCENTAGES OF ANTISTIPPING AGENTS

Some researches classified stripping as a physio-chemical incompatibility of an asphalt system [15]. They suggested that under saturated conditions all asphalt mixes may fail as a consequence of cyclical hydraulic stress physically scouring the asphalt binder from the aggregate. They classified such stripping as a mechanical failure of the asphalt pavement system and the classical moisture sensitivity tests are irrelevant. Their study documented four such case histories from Pennsylvania, Oklahoma, and New South Wales in Australia. Case histories gave the details of construction, visual observation of pavement distress, sampling and testing of pavement, conclusions and recommendations. Moisture profile within the pavement structure was also determined by dry sampling with a jack hammer. The phenomenon of stripping was investigated from a global perspective, looking at the relative permeability of the pavement components, subsurface drainage system, and the interaction between different asphalt courses including open-graded friction courses. Hypotheses were presented to explain the mechanisms that result in the pavement saturation. They recommended using the percentage of lime as 1-1.5% in the Hot Mix Asphalt (HMA).

5. ELVALOY PLASTOMER

Elvaloy is a type of plastomer and used in almost 32 states in the USA to modify base asphalt binder. Elvaloy for this study was collected from DuPont, USA and is suitable for very hot (Arizona) to very cold (Wisconsin) places. Its molecular structure shows the presence of n-Butyle Acrylate and Glycidyl Methacrylate i, e (mainly Ethylene -CH₂).

Elvaloy is made of ethylene glycidyl acrylate (EGA) terpolymer that chemically reacts with the asphalt binder during mixing. The main advantage of the chemical reaction is that it helps the base asphalt binder not from separating from the Elvaloy during storage and transportation. Asphalt roads using Elvaloy have been in use since 1991. In 1995 Witezak [16] studied the laboratory performance of asphalt modified with Elvaloy. Two different grades of asphalt were each modified by 0%, 1.5% and 2.0% Elvaloy by weight of binder. The susceptibility of the mixtures to moisture damage was found to be greatly decreased by the addition of Elvaloy [17]. The Elastomeric used in this

study is polymer based and therefore it is classified as plastomeric modifier. It modifies asphalt binders by forming a tough, rigid, three-dimensional network to resist deformation. Its characteristics lie between those of low density polyethylene, semi rigid, translucent product and those of a transparent and rubbery material similar to plasticized poly vinyl chloride (PVC) and certain types of rubbers modifiers [18]. When added in small quantities to asphalt, Elvaloy creates a permanently modified binder with improved elastomeric properties. Unlike most other plastomers and elastomers that are simply mixed into asphalt, Elvaloy has an active ingredient that chemically reacts with asphalt. The result is not a mixture of asphalt and modifier, but rather a stable, elastically improved, more resilient binder that can be stored and shipped to hot mix plants to help meet Strategic Highway Research Program (SHRP) and other higher-performance specifications. Hot mix asphalts made with Elvaloy are easy to spread and compact, and provide outstanding resistant to rutting, cracking, and fatigue. Roads made with Elvaloy have been in service since 1991, and are showing excellent long-term durability.

Elvaloy as well as ethylene polymers are characterized by a low polarity and low reactivity plastomers. They are like waxes in this respect, having a low dielectric constant and being soluble in hot oils, hot wax and hot hydrocarbons. They also are well known to be inert. For some uses it is desirable to modify the ethylene polymers to make them flexible, to impart more polarity to the polymers, and to be able to use them in reaction with other resins. To obtain high degree of polarity (to improve the dispersion of these materials in asphalt) high level of ester are required, which in turn adversely affects the inherent advantage of the long ethylene chain (low cost, good temperature behavior, etc.) while retaining the hydrocarbon chain as the major feature of the polymer. Commercially available thermosetting resins such as phenolics, epoxys etc. have been found to be useful because of retention of their performance at elevated temperatures. This retention of performance is associated with the crosslinking or curing action inherent in the structure of the thermosetting resins utilized. However, this retention of high temperature performance is accompanied by high stiffness of such material or if some stiffness is desired by providing a higher degree of toughness. For these reasons Ecopath has developed the technology to blend flexible polymers into the thermosetting resin [19]. Research on Elvaloy modified binders show increased high temperature viscosities but they demonstrate limited viscosity changes at colder temperatures. As such, Elvaloy modified binder enhances the high temperature properties of the asphalt mix. The molecular arrangement of Elvaloy is shown in Figure 1 [19].

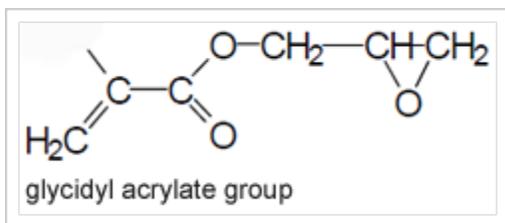


Figure 1. Elvaloy molecular arrangement [19]

The mixing percentage of Elvaloy is 2.0% and phosphoric acid is 0.25%. As phosphoric acid is a hygroscopic substance so it absorbs moisture from the air during operation and storage. At

the time of storage and handling of the acid, care is taken to avoid contact with water and air. Precautions must be taken during the dilution of phosphoric acid with water as this is highly exothermic chemical reaction. The acid dilution was carried out slowly in the current study. Dilution in water causes acid to be more aggressive on skin contact. A lab mix study needs to be performed to determine optimum Elvaloy® RET and acid levels prior to producing commercial pounds of product. It is not a good idea to increase polymer or acid levels above laboratory levels without first running a lab test to see if polymer modified asphalt produces gel at the increased levels of polymer and/or acid. DuPont has an asphalt laboratory that performed initial screenings of this process on your asphalt, and provided SHRP data for the asphalt.

6. ANTISTRIPPING AGENTS

Kling Beta (KB) is a brown color liquid (at 25 °C) consists of amines. It was supplied by Akzo Nobel Surface Chemistry, Texas. It does not have significant odor. A typical dose of 0.25-0.75% by weight of asphalt is recommended for use which should be determined in laboratory mix design tests. During plant mixing, Kling Beta is usually added to the asphalt binder by means of a specially designed injection system. Alternatively, it can be incorporated into the asphalt binder by mechanical agitation, pump circulation of the storage tank, or by injection into the asphalt loading line followed by recirculation through the truck bypass system until properly mixed. Usually flash point is 200°C. The viscosities of KlingBeta is 5500 mPa.s at 20°C and 1000 mPa.s at 40°C [20].

Lime has been added to hot mix asphalt pavements for over 25 years. The growth of the demand has been significant, currently totaling over 400,000 tonnes per year [21]. Lime contributes to both the mechanical and rheological properties of asphalt mixtures. Lime improves moisture sensitivity resistance and fracture toughness along with reducing the rate of oxidative aging of many asphalt binders. Considerable laboratory research has been performed to quantify the benefits of hydrated lime, and decades of field performance have validated the laboratory conclusions [22]. Antistripping additives are used to increase physico-chemical bond between the bitumen and aggregate and to improve wetting by lowering the surface tension of the bitumen [23, 24]. Stuart [25] tested (i) hydrated lime and quick lime, (ii) silane coupling agents, and (iii) silicone. Among them, hydrated lime and quicklime have shown to be the most effective antistripping agents [26, 27, and 28]. When lime is added to hot mix asphalt (HMA), it reacts with aggregate and strengthens the bond between the bitumen and the aggregate interface. Lime reacts with highly polar molecules to inhibit the formation of water-soluble soaps that promote stripping. When polar molecules react with lime, they form insoluble salts that no longer attract water. Lime contains mostly silicium dioxide and surface moisture. Table 1 shows the properties of hydrated lime.

7. CONDITIONING OF SAMPLES BY AASHTO T-283 METHOD

AASHTO T 283 method was applied to condition the samples. In this process De-Ionized water from the Chemistry dept (UNM) was used. About 500 ml De-Ionized water was put in the vacuum bottle and then the bottle on its side (but tilted up) with gravel holding it in place so that no water spills out. A few samples were placed in a jar with asphalt slide side up. With the

Table 1 Properties of hydrated lime [29]

Name	Formula	%
Silicium dioxide	SiO ₂	40%
Ferrous oxide+	Fe ₂ O ₃ ⁺	12%
Aluminum oxide	Al ₂ O ₃	10%
Calcium oxide	CaO	-
Magnesium oxide	MgO	-
Sulfur trioxide	SO ₃	-
Surface moisture	H ₂ O	40%

jar still on its side, the metal cap was put on it. It was critical that no water touches the hose outlet on the cap. Then the vacuum pump was run for 10 minutes so that air bubbles form in the water. After that the samples are left in the water for another 10 minutes. The samples are then removed from water, replaced any labels that came off, wrapped them in Seran wrap. Samples are placed in a ziploc bag, 10 ml DI water was added in the bag and sealed. Samples are then placed in a fridge -18°C for a minimum of 16 hours. After 16 hours, the samples are removed and all plastic wrappings are cut and placed in a hot water bath for 10 hours. Samples were wiped using a damp towel to remove excess surface water and placed in the oven at 27°C for 2 hours. After complete conditioning, samples are dried. Next samples were put inside an oven to ensure no water on the asphalt sample surface. All binders slide samples were kept in oven for 8 hours at 40°C.

8. AFM TESTING

Figure 2 shows the AFM used in this study. In AFM testing, a cantilever scans the asphalt film with a small and sharp tip placed at the free end of the cantilever. The deflection of the cantilever, describing the interaction between the AFM tip and the asphalt surface, is monitored by an optical lever method combined of laser diode and position sensitive photo detector. Based on the deflection δ and the stiffness k of



Figure 2. AFM picture

the cantilever, the force F acting on the AFM tip is obtained from, $F = k \delta$. By measuring the deflection of the cantilever tip, a topographic image of the surface is obtained. Next, image is

analyzed to determine surface roughness. If the surface roughness is smaller 25 nm (nano meter), sample surface is considered as smooth, therefore suitable for adhesion testing. Adhesion is defined as the force between atoms of an AFM tip and atoms of asphalt binder. It can be thought as a pull-off force at molecular level. The main AFM setup is shown in Figure 2 It has a microscope, steel cap, noise reduction chamber and tip holder.

A clean room is a low level of environmental pollutants i, e., dust, airborne microbes, chemical vapors and aerosol particles. All of our AFM experiments were done in a cleanroom inside Center for High Tech Materials (CHTM) as shown in Figure 3. The problems associated with molecular and particle contamination of spacecraft components, instruments and structures are well known and documented especially those that contain fine mechanisms and/or optics. This problem is severely exaggerated when the instrument is operating under space vacuum. A Class 10 cleanroom is defined as having less than 10 particles of more than 0.5 micron in size within a cubic foot of air. Similarly, a Class 1000 cleanroom has less than 1000 particles of more than 0.5 micron in size within a cubic foot of air. This level of cleanliness is necessary to maintain the reproducibility of newly developed state-of-the art electronic device processes. To reach and maintain this level of cleanliness, the transfer of particle and chemical contaminations must be eliminated wherever they are found.



Figure 3. Picture of clean room at CHTM

9. ASPHALT FILM PREPARATION

The actual picture of an AFM sample is shown in Figure 4. At first, a thin glass slide surface was wrapped with tape. A small

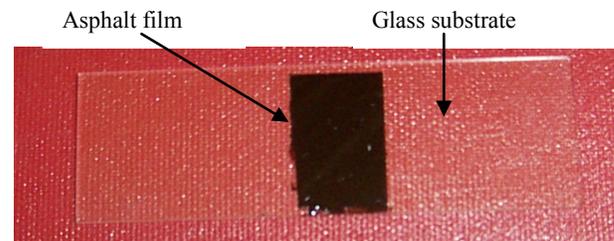


Figure 4. Actual asphalt film on glass substrate

portion of asphalt was placed in an oven and then heated at 163°C temperature. Next, the hot liquid asphalt was poured in the gap between two slices of tape on glass. The surface of the liquid asphalt was leveled to the surface of tape by rubbing it with a cleaned spatula. The asphalt on glass was then left for cooling and finally the tapes were peeled off. To this end the dry sample was ready for AFM testing.

10. TEST MATRIX

In this study the PG 58-28 (base) binder was modified with 0.5%, 0.75%, 1.5% and 2% Elvaloy. Each of the five binders was mixed with the three percentages (0.25%, 0.5% and 0.75%) of anti stripping agent Kling Beta and Lime to investigate moisture damage in asphalt film. Each of the binders was tested after dry and wet conditioned. Each sample was tested at four different locations on the film surface. Four different functionalized AFM cantilever tips were used. Therefore, the test matrix involves a total of 960 tests (2 moisture conditions x 5 PG binders x 2 types of anti stripping agents x 3 percentages of anti stripping agents x 4 cantilever tips x 4 locations).

11. AFM TEST PARAMETERS

Traditionally, AFM tests are conducted mostly on hard samples to measure surface roughness. As asphalt samples are relatively soft compared to typical silicon or metal samples, the AFM test on asphalt becomes non-trivial, especially when considering the stickiness of asphalt binder. Therefore, several parameters are controlled carefully in this study to minimize the contact between the tip and asphalt surface. The final values of these parameters for successful AFM testing on asphalt sample are listed in Table 2.

Table 2 The AFM Testing Parameters

AFM Parameters	Values
Set Point	-0.12 to -0.51
Scan Area (A° x A°)	40 x 40
Scan Rate (Hz)	3
Amplitude	25 to 40

It can be noted that the AFM is set up at a minus value to ensure that tip is not in contact with sample surface. Essentially tests are performed at non-contact mode with tip vibration off. During scanning or surface imaging, the AFM is setup in high voltage mode. A scan rate between 1 and 3 Hz is found to produce high quality images. Scan rate is defined by the frequency of the back and forth movements of the scanner beneath the AFM probe. It can be mentioned that setting up an appropriate scanning rate is important for capturing a good quality image. If a sample is scanned at a very fast rate, the feedback loop may not have enough time to respond to the change in film roughness, and hence may result in a bad quality image or smeared image [30]. A slow scan rate produces a good resolution of the image as the feedback system finds enough time to respond, while a fast scan rate can be time efficient. In this study, a total of 256 x 256 pixels are used to scan 5- μm^2 of the sample. The gain value is set 0.1 for all the tests. The gain value controls the error signal to generate a feedback signal.

12. AFM TIP CALIBRATION

The AFM system requires performing the calibration procedure whenever switches to a different cantilever probes. However, the system remembers the calibration results, so no need to repeat the procedure whenever to exit the main image processing Proscan software. Before starting imaging calibration it is necessary to calibrate the vertical axis of the F vs. d graph with units of force. The spring constant should be calibrated and used to get the correct force values from the AFM [3, 4]. The calibration procedure involves taking a Force vs. distance curve using a hard sample such as the available calibration grating supplied with the AFM system [24]. Hard sample ensures the mechanical properties of the sample do not couple with those of the cantilever and affect the calibration. The whole procedure involves three general steps: To check or enter the value of the cantilever force constant, Acquire an F vs. d curve and Run an automated procedure that performs the calibration. The cantilever force constant is a database parameter and the correct force constant value already loaded in the software database. The requirement of F vs. d curve generates for the calibration procedure should be well behaved and there should be a substantial portion of the linear part of the curve to be visible, the part that represents deflection of the cantilever once contact is made with the sample. Using the mouse to select two points on this linear portion of the curve so that the system may use these points to calculate a slope value, which is used along with the force constant to calibrate volts with units of force. To obtain adhesion force values, it is required to know the exact value of the cantilever spring constants (k) of the functionalized tips. This is done through the automated tip calibration procedure (AFM Part 00-103-0990 module) available in the AFM control software. In the calibration procedure, the cantilever to be calibrated (i.e., a functionalized tip) is used to measure force curves on a platinum-coated hard sample (calibration grating, Model APCS -0001) and on a reference cantilever. The slope of the contact portion of the force curve is called stiffness, S. Thus two quantities: S_{ref} which is the deflection sensitivity of the reference cantilever, and S_{hard} which is the deflection sensitivity of the hard surface are measured. Whereas the spring constant of the reference cantilever, k_{ref} is known. The calibrated k value is determined from the following equation [32]:

$$k = \left(\frac{S_{ref}}{S_{hard}} - 1 \right) k_{ref} \quad (1)$$

In this study, the calibrated values of the cantilever spring constants are determined to be: $k_{ref} = 3.0$ N/m, $k_{Si_3N_4} = 3.9564$ N/m, $k_{COOH} = 5.0889$ N/m, $k_{OH} = 3.433$ N/m, $k_{CH_3} = 3.121$ N/m and $k_{NH_3} = 2.428$ N/m.

13. FUNCTIONALIZED TIPS

The tips were fictionalized with carboxyl (-COOH), methyl (-CH₃), ammin (-NH₃) and hydroxyl (-OH) groups from the help of Novascan Technologies, Ames, IA. These functionals are known to be a major part of asphalt chemistry [33]. The microscopic images of asphalt film were analyzed using Proscan 1.6 Software and WSXM software [34]. A 5 μm^2 area scanner was used to scan asphalt samples in high voltage mode. A total of 256 x 256 pixels were used for output image. During scanning the asphalt film are kept in an enclosed chamber to minimize the samples and tips for interference from air and other noise. In this study, the AFM testing was conducted in two modes: contact and non-contact modes. In imaging, non-contact

mode was employed, whereas contact mode was employed for adhesion testing. Non-contact mode has advantage over the contact mode for imaging soft samples [35].

14. DESCRIPTION OF A FORCE DISTANCE CURVE

A generalized force-distance curve from the AFM testing is shown in Figure 5. The horizontal axis shows the vertical movement of cantilever tips and the vertical axis shows the force (+ve as repulsive, and -ve as attractive) acting between tip molecule and asphalt molecule. When the tip is at a large distance from the sample, no force is found to act between the tip and surface. But as the tip approaches, the distance decreases and the attractive forces cause to pull the cantilever tip towards the sample. At the time of approaching (shown in the path A-B-C) the cantilever deflects away from the surface. As the tip approaches close to the sample the value of the attraction force increases and becomes the maximum at a certain distance. The force is theoretically very high when the tip touches the sample. After that the tip starts withdrawn back to its original position.

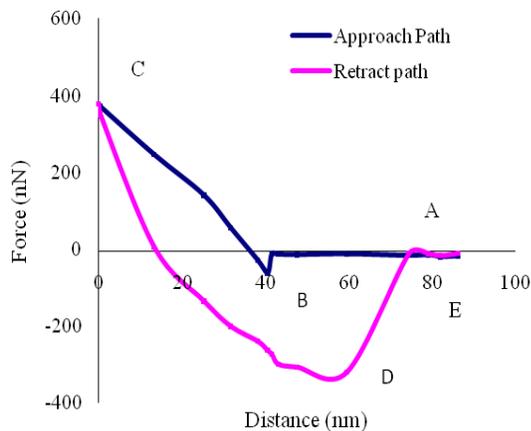


Figure 5. Force distance curve from the AFM experiment with – COOH tip

While on the retracting path (Path C-D-E), the tip sticks to the surface for considerable distances because of the bonds formed during contact with the surface. At a certain point, it finally snaps out of contact from the sample surface. As the cantilever tip travels away from the sample, it deflects towards the surface due to adhesion force between the sample and tip. Finally, the cantilever tip separates itself from the sample surface, where the lowest point (point D) in retracting path or curve occurs. Upon further separation from the lowest point (moving right from left along the retracting path), the tip completely loses contact with the surface, and jumps out of the sample surface. The maximum force between tip and sample at the lowest point in Figure 5 (point D) is referred to as the adhesion force or pull-off force. Adhesion between the tip and the sample is mainly due to van der Waals interactions [36].

15. AFM IMAGES

The AFM images of dry and wet samples are shown in Figure 6. It can be seen that the wet sample has no more regular shape (spikes) like the dry samples. The spikes are seems to be eroded by some external forces. This can be assumed as the adverse effect of moisture on the asphalt binder surface.

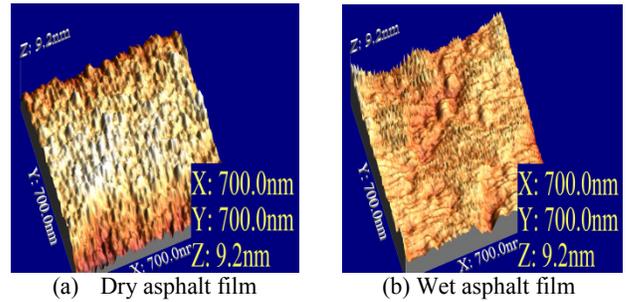


Figure 6. 3D AFM image of AFM samples

16. STATISTICAL ANALYSIS OF AFM DATA

Statistical analysis is important in order to resolve issues involve the study of data analysis. Statistics has been described as the scientific and mathematical study of data. In a very large datasets or database, it is impossible and impractical to analyze every piece of data very quickly. Hence, a sample of the data is studied and the rest of the data results can be extrapolated from the sample data.

A test result from experiment will be called statistically significant if it is unlikely to have occurred by chance. But the word significant does not mean important or meaningful. It represents the true state of experimental data. The popular levels of significance are defined as 5% (0.05), 1% (0.01) and 0.1% (0.001). If a test of significance gives a p-value lower than the α -level, the null hypothesis is rejected. Typically a null hypothesis suggests a general position, such that there is no relationship between two measured occurrence or phenomena or that a potential treatment has no effect. Such results are informally referred to as 'statistically significant'.

P- value

Table 3 shows the results. In statistical significance testing, the p-value is the probability of obtaining a test statistic at least as extreme as the one that was actually observed, assuming that the null hypothesis is true. The lower the p-value, the less likely the result is if the null hypothesis is true, and consequently the more "significant" the result is, in the sense of statistical significance [38]. One often accepts the alternative hypothesis, (i.e. rejects a null hypothesis) if the p-value is less than 0.05 or 0.01, corresponding respectively to a 5% or 1% chance of rejecting the null hypothesis when it is true. In this study we did analyze all the P value for the output data. All the values found to be less than 0.001 which is the expected values. This suggests that the all test outputs are significant.

Pearson Value

Statistical analysis of adhesion values is performed to find product-moment correlation coefficient. It is a measure of the correlation (or linear dependence) between two different variables [37]. In this study, these two variables are adhesion and % antistripping agents. Table 3 shows the results. The output is a value between -1 and +1. The value close to +1 indicates the strong linear proportional relations between the output and input data. The value close to -1 indicates the strong inverse proportional relation between input and output data. It is widely used in the engineering as a measure of the strength of linear dependence between two variables. The tests were accomplished with all the tips. The Pearson values for dry and wet samples of 0.5% Elvaloy modified with KB is 0.9303 which is very close to +1. This is shows a strong correlation between

output and input data. The wet 0.75% Elvaloy modified with KB samples Pearsons value is 0.5891 which is may be indication of the adverse water effect that took place on the wet samples.

Table 3. Statistical analysis results of KB modified samples.

Tip	Elvaloy %	Condition	Antistripping Agent (KB%)	P-value	Pearson value
-COOH	0.75	Dry	0.25	0.0000245	-0.0935
			0.5		
			0.75		
		Wet	0.25	0.0000210	0.5891
			0.5		
			0.75		
-OH	0.5	Dry	0.25	0.0020169	0.9303
			0.5		
			0.75		
		Wet	0.25	0.0000062	-0.3907
			0.5		
			0.75		
-NH3	1.5	Dry	0.25	0.0000599	-0.9534
			0.5		
			0.75		
		Wet	0.25	0.0065912	-0.3521
			0.5		
			0.75		
-CH3	2	Dry	0.25	0.0000539	0.8147
			0.5		
			0.75		
		Wet	0.25	0.0000186	0.9952
			0.5		
			0.75		

17. ADHESION VALUES COMPARIOSN FOR THE SAMPLES

Table 4 shows the change in adhesion results for the lime modified samples with all the -COOH, -NH3, -CH3 and -OH tips. Here the only percentage changes in dry and wet samples are used to calculate the values. The adhesion loss or change is calculated from the dry and wet adhesion values. All the values are positive which indicate the moisture damage in asphalt binder. The values are with -COOH tip is very low, less than about 20nN for most of the cases. With the -NH3, -CH3 and -OH tips the values are higher than that of -COOH tip.

Table 5 shows the change in adhesion results for the KB modifies samples. All the values are positive which indicate the moisture damage in asphalt binder in presence of KB antistripping agents. The values are with -COOH tip are very high as compared to that with lime modified samples. The % change is more than 50nN for most of the cases. The changes with the -NH3, -CH3 and -OH tips are not much different than that of lime modified samples.

Table 4. The % changes of adhesion forces (nN) of dry and wet samples for the lime modified samples

Sample	% Changes of adhesion			
	-COOH	-NH3	-CH3	-OH
El 0.5%: Lm 0.5%	26.90	75.28	175.85	120.68
El 0.5%: Lm 1.0%	32.33	97.67	193.22	69.23
El 0.5%: Lm 1.5%	27.03	128.57	55.83	169.15
El 0.75%: Lm 0.5%	9.35	56.76	168.51	138.60
El 0.75%: Lm 1.0%	12.76	68.86	113.14	55.37
El 0.75%: Lm 1.5%	23.42	19.27	54.77	93.81
El 1.5%: Lm 0.5%	2.35	19.43	114.75	20.16
El 1.5%: Lm 1.0%	6.05	12.09	253.01	30.73
El 1.5%: Lm 1.5%	3.90	3.52	125.99	35.03
El 2.0%: Lm 0.5%	18.45	25.86	178.39	87.01
El 2.0%: Lm 1.0%	11.09	44.12	162.90	168.33
El 2.0%: Lm 1.5%	12.04	24.00	503.01	10.96

Table 5. The % changes of adhesion forces (nN) of dry and wet samples for the KB modified samples

Sample	% Changes of adhesion			
	-COOH	-NH3	-CH3	-OH
El 0.5%: KB 0.25%	64.88	70.84	57.06	99.33
El 0.5%: KB 0.5%	135.30	55.78	32.48	17.40
El 0.5%: KB 0.75%	285.69	63.03	19.63	18.04
El 0.75%: KB 0.25%	10.28	129.18	45.92	35.66
El 0.75%: KB 0.5%	48.11	163.56	68.10	79.67

Table 5 The % changes of adhesion forces (nN) of dry and wet samples for the KB modified samples (continue)

Sample	% Changes of adhesion			
	-COOH	-NH ₃	-CH ₃	-OH
El 0.75%: KB 0.75%	22.58	144.56	62.17	55.87
El 1.5%: KB 0.25%	28.27	51.63	56.81	31.80
El 1.5%: KB 0.5%	29.10	37.93	71.33	46.55
El 1.5%: KB 0.75%	53.44	49.21	54.92	65.51
El 2.0%: KB 0.25%	78.34	35.57	48.13	8.59
El 2.0%: KB 0.5%	232.26	93.92	32.06	7.31
El 2.0%: KB 0.75%	68.20	79.65	45.80	7.58

Effect of Kling Beta on moisture damage

Using the -OH tip: The change in adhesion forces of dry and wet samples of 0.5% Elvaloy is shown in Figure 7. The adhesion at three percentages of KB binder using -OH tip are plotted. It is seen that the 0.5% and 0.75% KB are more effective to prevent the moisture damage as they have the least change in adhesion force. At 0.25% KB, there is a sharp increase in adhesion of wet conditioned samples. Therefore, it can be said the Kling Beta should not be used less than 0.5%.

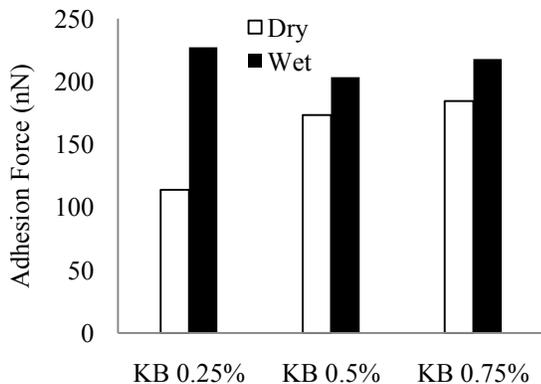


Figure 7. The change of adhesion forces on 0.5% Elvaloy and three percentages of KB with -OH tip

Using the -CH₃ tip: Figure 8 shows the effect of mixing KB on moisture damage based on the adhesion value measured using -CH₃ tips. The base binder was modified with

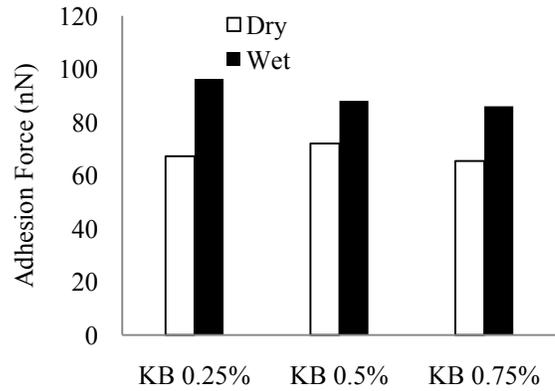


Figure 8. The change of adhesion forces on Base (PG 58-28) and three percentages of KB with -CH₃ tip

three percentages of KB here. Here 0.5% KB is the most effective to prevent the moisture as it has the lowest amount of increase in adhesion due to wet conditioning. The 0.25% KB has the worst performance against moisture damage. The performance of 0.75% KB is in between 0.25% KB and 0.5% KB.

Using the -NH₃ tip: Figure 9 shows the adhesion force results when the 0.5% Elvaloy modified binder was tested with the -NH₃ tip. Here 0.5% and 0.75% KB modifications are more effective than the 0.25% KB modification. Hence 0.5%~0.75% KB is suitable when designing the AC mix for preventing moisture damage.

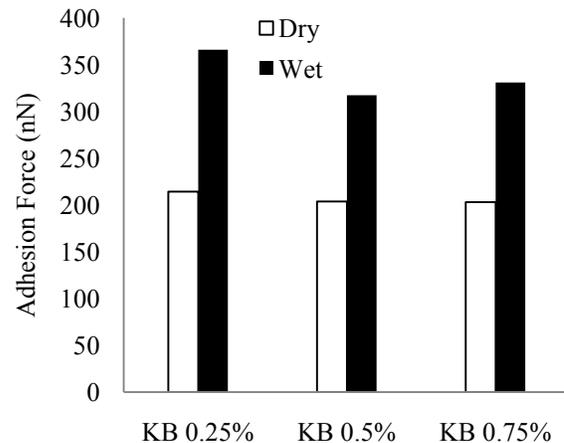


Figure 9. The change of adhesion forces on 0.5% Elvaloy and three percentages of KB with -NH₃ tip

Using the -COOH tip: The presence of -COOH functional is the most abundant in modified asphalt surface that is why the -COOH tip is showing the highest amount of adhesion force as compared to other tips [36]. But considering the effect of KB on moisture damages, this study is unable to reach any conclusion.

Effect of Lime on moisture damage

Using the -OH tip: Figure 10 shows the results on 0.75% Elvaloy modified samples with three percentages of lime using -OH tip. Here all the wet samples are gone through damages due to moisture action. It can be seen that at 1.5% lime,

there increase in adhesion in wet sample is very high compared to others.

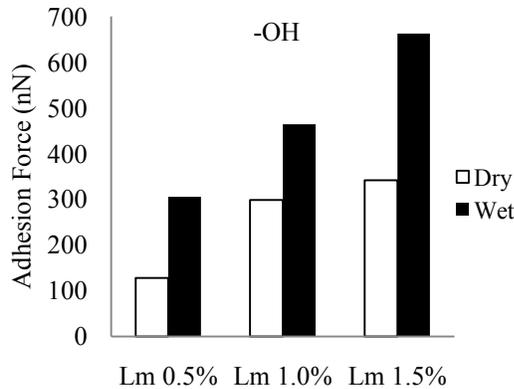


Figure 10. The change of adhesion forces on 0.75% Elvaloy and three percentages of Lime with –OH tip

Using the –CH₃ tip: Figure 11 shows the results on 0.5% Elvaloy modified samples. It can be seen that all the wet samples have suffered moisture damage. The wet adhesion forces are higher than that of dry samples.

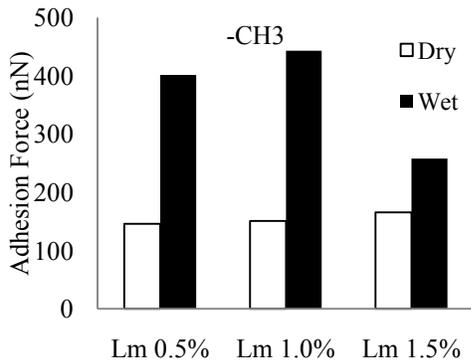


Figure 11. The change of adhesion forces on 0.5% Elvaloy modified samples and three percentages of Lime with – CH₃ tip

Using the –NH₃ tip: Figure 12 shows the results on 1.5% Elvaloy modified samples. Here all the wet samples experienced moisture damage. The 1.5% lime modification is the best to fight against moisture as compared to other used percentages here.

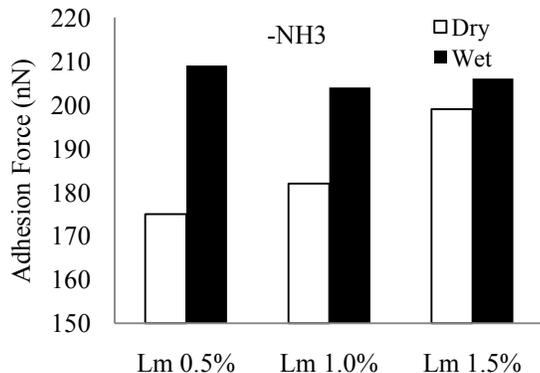


Figure 12. The change of adhesion forces on 1.5% Elvaloy modified samples and three percentages of Lime with – NH₃ tip

18. CONCLUSIONS

This study introduces the use of functionalized AFM tips to determine the moisture damage in plastomeric polymer modified asphalt binder with and without antistripping agents. The following conclusions are made:

- Statistical analysis of the AFM data shows that laboratory test data are significant for percent polymers and antistripping agents.
- Plastomeric modification does not help reduce adhesion, that is moisture damage, in asphalt binder.
- Antistripping agents can be used to prevent the damage. About 0.5% to 0.75% Kling Beta type antistripping agent is very effective to prevent moisture damage.
- The adhesion losses are less with the lime modification as compared to Kling Beta modification. In other words, lime is better than Kling Beta as an antistripping agent.

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20. REFERENCES

- [1] H. Shin-C., T. Turner, A. Pauli, F. Miknis, F. Branthaver, and R. Robertson, "Evaluation of Different Technique for Adhesive Properties of Asphalt-Filler Systems at Interfacial Region", **Journal of ASTM International**, Vol. 2, No. 5, 2005, pp. 1-15.
- [2] M.H. Sadd, Q. Dai, V. Parameswaran, and A. Shukla, "Simulation of Asphalt Materials Using a Finite Element Micromechanical Model with Damage Mechanics." **Transportation Research Board**, 1832, 2003, pp. 86-95.
- [3] D. Cheng, D. Little, R. Lytton, and J. Holste, "Use of Surface Free Energy Properties of the Asphalt-Aggregate System to Predict Moisture Damage Potential". **Journal of the Association of Asphalt Paving Technologists**, Vol.71, 2002, pp. 59-88.
- [4] E. Masad, A. Castelblanco, and B. Birgisson, "Effects of Air Void Size Distribution, Pore Pressure, and Bond Energy on Moisture Damage." **ASTM Journal of Testing and Evaluation**, Vol 34, Issue 1, 2006, pp. 9-16.
- [5] D. Little, and D. Jones, "Chemical and Mechanical Mechanisms of Moisture Damage in Hot Mix Asphalt Pavements." **National Seminar in Moisture Sensitivity**, San Diego, California, 2003.
- [6] N. Wasiuddin, M. Zaman, and E. O'Rear, "Effect of Sasobit and Aspha-Min on Wettability and Adhesion

- Between Asphalt Binders and Aggregates.” **Journal of Transportation Research Board**, TRB, Vol. 2051, 2008, pp. 80-89.
- [7] S. Huang, T. Turner, A. Pauli, F. Miknis, J. Branthaver, and R. Robertson, “Evaluation of Different Techniques for Adhesive Properties of Asphalt-Filler Systems at Interfacial Region.” **Journal of ASTM International**, vol. 2, no. 5, 2005, pp. 1-15.
- [8] R. Hicks, R. Leahy, M. Cook, J. Moulthrop, and J. Button, “Road Map for Mitigating National Moisture Sensitivity Concern in Hot Mix Pavements.” **83rd Annual Meeting of Transportation Research Board**, National Res. Council, Washington D.C., 2004.
- [9] R. Hicks, “Moisture damage in asphalt concrete.” NCHRP synthesis of highway practice 175, Washington (DC): **Transportation Research Board**, National Research Council, 1991.
- [10] R. Lottman, “Predicting Moisture-Induced Damage to Asphalt Concrete – Field Evaluation.” **Transportation Research Board**, NCHRP Report 246, 1982.
- [11] Transportation Research Board (TRB), Moisture Sensitivity of Asphalt Pavements, **National Seminar**, San Diego, California, February 2003.
- [12] B. Huang, X. Shu, Q. Dong, and J. Shen, “Laboratory Evaluation of Moisture Susceptibility of Hot-Mix Asphalt Containing Cementitious Fillers.” **Journal of Materials in Civil Engineering**, ASCE, 2010, pp 667.
- [13] P. Sebaaly, H. Hitti, and D. Weitzel, “Effectiveness of Lime in Hot Mix Asphalt Pavements.” **82nd Annual Meeting of the Transportation Research Board**, November 12, 2002.
- [14] B. Putman, and S. Amirkhani, “Laboratory Evaluation of Anti-Strip Additives in Hot Mix Asphalt.” **Report No. FHWA-SC-06-07**, South Carolina Department of Transportation, November 10, 2006.
- [15] P. Kandhal and I. Rickards, “Premature Failure of Asphalt Overlays from Stripping: Case Histories.” NCAT Report 01-01, **Annual meeting of the Association of Asphalt Paving Technologists**, Clear Water, Florida, March 19-21, 2001.
- [16] M. Witzak, I. Hafez, and X. Qi, “Laboratory characterization of Elvaloy® modified asphalt mixtures: vol. I – Technical report.” College Park, Maryland: University of Maryland. **Available from website: Dupont website accessed on November 2010.**
- [17] Y. Yelderim, “Polymer modified asphalt binders.” **Construction and Building Materials**, Vol 21, No. 1, 2007, pp 66-72.
- [18] P. Mahabir, and M. Mazumdar, “Engineering properties of EVA modified bitumen binder for paving mixes.” **J Mater Civil Eng**, 11(2), 1999, pp 131-137.
- [19] Ecopath website, <http://www.ecopathindustries.com/index.php?option=com_content&view=article&id=87&Itemid=94> (September, 2010)
- [20] Akzo Nobel handbook, 2006.
- [21] USGS Annual Commodity Mineral Yearbook, Lime, Table 4, 2004.
- [22] Berger and Huege (2005), <www.internationallime.org/doc/BERGER%20Eric.doc> (September, 2010)
- [23] K. Majidzadeh, and F. Brovold, “Effect of Water on Bitumen-aggregate Mixtures.” **Highway research board special report**, 98, 1968.
- [24] E. Hunter, “Evaluating moisture susceptibility of asphalt mixes.” **MPC report**. University of Wyoming, WY, 2001.
- [25] K. Stuart, “Moisture Damage in Asphalt Mixtures: a State of Art Report.” **Research Development and Technology**, Turner-Fairbank Highway Research Center, 1990.
- [26] A. Zvejnicks, “Progress with Adhesion – Improving Bitumen Additives.” **Highway Res Board Bull**, 192, 1958, pp 26-32.
- [27] C. Petersen, H. Plancher, and M. Harnsbergen, “Lime Treatment of Asphalt to Reduce Age Hardening and Improve Flow Properties.” **In: Proceedings, AAPT**, vol. 56, 1987.
- [28] T. Kennedy, and N. Anagnos, “Lime Treatment of Asphalt Mixtures.” **Center for Transportation Research**, The University of Texas at Austin, 1983, pp 20-8.
- [29] C. Gorkem, and B. Sengoz, “Predicting stripping and moisture induced damage of asphalt concrete prepared with polymer modified bitumen and hydrated lime.” **Construction and Building Materials**, 23, 2009, pp 2227-2236.
- [30] R. Thomas, J. Houston, R. Crooks, T. Kim, and T. Michalske, “Probing Adhesion Forces at the Molecular Scale.” **Journal of the American Chemical Society**, 117, 1995, pp 3830-3834.
- [31] J. Cleveland, S. Manne, D. Bocek, and P. Hansma, “A nondestructive method for determining the spring constant of cantilevers for scanning force microscopy”, **Rev. Sci. Instrum.**, Vol. 64, No 2, 1993.
- [32] B. Ohler, “Cantilever spring constant calibration using laser Doppler vibrometry”. **Rev. Sci. Instrum.**, Vol. 78, No. 06370, 2007, pp 1-5.
- [33] S. Testa, “Chemical Aspect of Cold-Mix Asphalt Incorporating Contaminated Soil”. **Journal of Soil Contamination**, Vol. 4, No. 2, 1995, pp 1-17.
- [34] I. Horacos, R. Fernandez, J. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, and A. Baro, “WSXM: A software for scanning probe microscopy and a tool for nanotechnology”. **Review of Scientific Instruments**, Vol. 78, Issue 1, 2007, pp. 013705-013708.
- [35] N. Jalili, M. Dadfarnia, and D. Dawson, “A Fresh Insight Into the Microcantilever-Sample Interaction Problem in Non-Contact Atomic Force Microscopy”, **Journal of Dynamic Systems, Measurement, and Control**, Vol. 126, 2004, pp. 327-335.
- [36] D. Vezenov, A. Noy, and C. Lieber, “Chemical Force Microscopy: Force Spectroscopy and Imaging of Complex Interactions in Molecular Assemblies”, **Handbook of Molecular Force Spectroscopy**, Springer US, 2008, pp 123-141.
- [37] J. Cohen, P. Cohen, S. West, and L. Aiken, **Applied multiple regression/correlation analysis for the behavioral sciences, (3rd ed.)** Psychology Press, 2002.
- [38] A. Desrosières, **The Politics of Large Numbers: A History of Statistical Reasoning**. Trans. Camille Naish. Harvard University Press, 2004.