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

Rafiqul TAREFDER

Assistant Professor
Department of Civil Engineering, University of New Mexico,
Albuquerque, NM 87131-0001, USA
and

Md ARIFUZZAMAN
PhD Candidate
Department of Civil Engineering, University of New Mexico,
Albuquerque, NM 87131-0001, USA

ABSTRACT

In this study, four different percentages of plastomeric polymer modified asphalt binders are used to investigate the moisture damage using the Atomic Force Microscopy (AFM). The force distance mode of AFM is used to measure the adhesion forces between the asphalt surface and functionalized AFM tips. Asphalt binders are mixed with three different percentages of antistripping agents to evaluate the nanoscale performance of the modified binders against moisture damage. AASHTO T-283 method is used for wet conditioning of asphalt samples. The main functional (chemical) group of asphalt binder (-COOH, -CH_3, -NH_3, and –OH) are used to functionalize the AFM tips to simulate the results with field performance. The AFM tips are calibrated with special AFM tip calibration module to achieve the correct adhesion force values and to quantify the nature and extent of the moisture damage. The adhesion force values showed significant deference when compared between the conditioned and dry samples. Among the functional groups, the -CH_3, -NH_3, and –OH showed some good results. But the functional group –COOH does not represent any decisive conclusions for adhesion loss/gain due to moisture and optimum antistripping agent. The results from this study can be useful to identify the mechanisms for the asphaltic pavements moisture damage from the nanoscale point of view.

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

1. INTRODUCTION

Adhesion force of asphalt binder is an important factor for understanding moisture damage behavior of asphalt concrete (AC). So far, adhesion force between asphalt and aggregate has been determined largely at macro-level. The macro-level adhesion lacks in explaining moisture damage in AC. Very recently some research have done adhesion test on asphalt film using Atomic Force Microscopy (AFM). However their study was limited to silicon tip [1]. This 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 two tasks: one is to capture the microscopic image of asphalt film and measurement of the roughness of film surface with AFM, the other is to determine the moisture damage effect when the antistripping agents are mixed with plastomer modified binder.

2. ELVALOY PLASTOMER

Elvaloy is a plastomeric polymer and used in almost 32 states in the USA to modify the base asphalt binder. It 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 Acrylet and Glycidyl Methacrylate (mainly Ethylene –CH_2).

3. ANTISTRIPPING AGENT (KB)

Kling Beta is a brown color liquid antistripping agent that contains amines. This chemical is used widely in US and all over the world to prevent stripping in AC. It has flash point of about 200°C and Viscosity of 450 mPa.s at 50°C. The typical use of KB antistripping agent is 0.25% to 0.75% by weight of asphalt, depending on the aggregate and asphalt type.

4. CONDITIONING OF SAMPLES BY AASHTO T-283 METHOD

The asphalt samples went through some standardized freezing and thawing procedure called AASHTO T-283. De-ionized water was used in this procedure to avoid the foreign materials that may deposit on the sample surface, which have detrimental effects on AFM results. All dry samples are vacuumed for 10 minutes in the vacuum jar to drive the air bubble from the samples. Then they were placed in the fridge at 0°C for 16 hours. After that the samples were kept in hot water bath at 60°C for 10 hours. Then they were placed in oven at 40°C over night to drive out all the moisture.

5. PRINCIPLES OF AFM TESTING

Figure 1 presents the schematic diagram of an AFM test setup. 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 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.

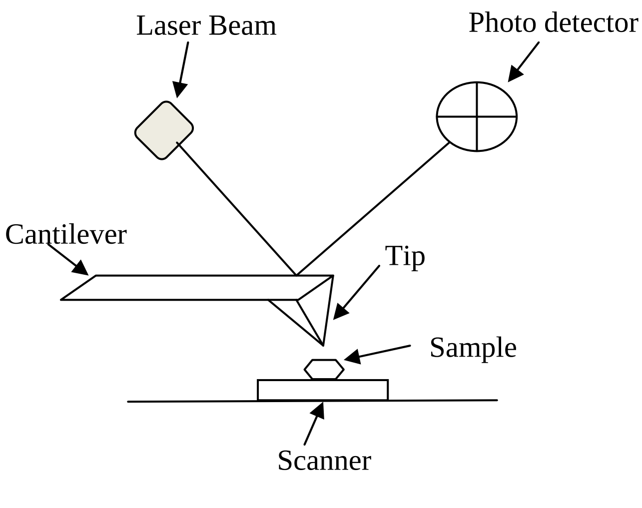


Figure 1. Schematic of an AFM [2]

6. ASPHALT FILM PREPARATION

A photograph of an AFM sample is shown in Figure 2. To prepare this sample at first, a thin glass slide surface was wrapped with tape. A small 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.

7. 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 were mixed with three percentages (0.25%, 0.5% and 0.75%) of anti stripping agent Kling Beta 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 480 tests (2 moisture conditions x 5 PG binders x 3 anti stripping agents x 4 cantilever tips x 4 locations).

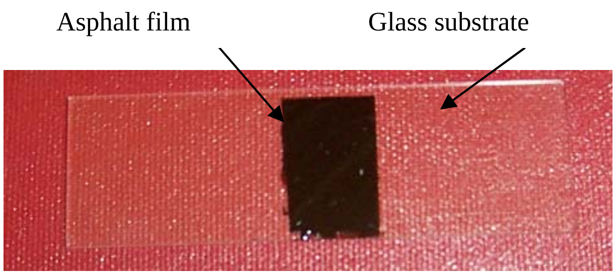


Figure 2. Actual asphalt film on glass substrate

8. 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 is 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. 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.

9. FUNCTIONALIZED TIPS

AFM tips were fictionalized using carboxyl (-COOH), methyl ($-CH_3$), ammin ($-NH_3$) and hydroxyl (-OH) groups from the help of Novascan Technologies, Ames, IA. These functionals are known to be a major part of asphalt chemistry [5]. The microscopic images of asphalt film were analyzed using Proscan 1.6 Software and WSXM software [6]. 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, but not for adhesion measurement [7].

10. DESCRIPTION OF A F-D CURVE

A Force-Distance curve from the AFM testing is shown in Figure 4. 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 and asphalt sample. As the tip is very far from the sample we cannot see any force to act between the tip and surface. But as the tip start approaching, the distance is decreasing and the attractive forces causing the cantilever tip to pull towards the sample. At the time of approaching (shown in the blue line path) 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. While on the retracting path (shown in the red line path), 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 4 **(**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 [8].

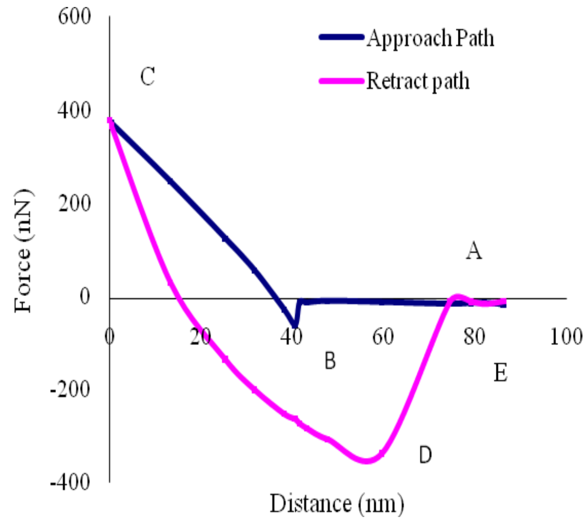
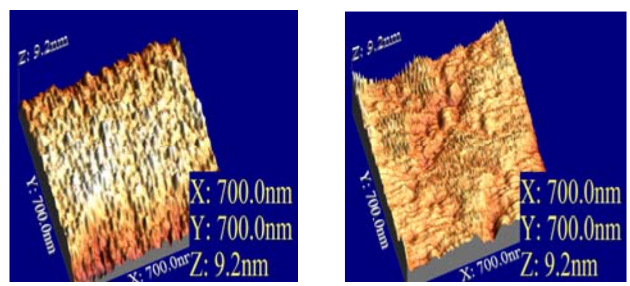


Figure 4. An actual F-D curve from the AFM experiment using –COOH tip

11. AFM IMAGES

The AFM images of dry and wet samples are shown in Figure 3. 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.



(a) Dry asphalt film (b) Wet asphalt film

Figure 3. 3D AFM image of AFM samples

12. RESULTS

The results of the average of four points tests as well as the rate of change of cohesion forces are shown in Table 1. It can be seen that all most all the wet samples cohesion forces are noticeably higher than that of dry samples. The water action has made the samples softer to an extent and as a result the samples are holding the AFM tip strongly at the time of separation from the sample (on the retracting path of Figure 4).

Table 1. The four point average cohesion forces (nN) of dry and wet samples and their changes with different tips

	Dry				Wet				% of Change [(Wet-Dry)/Dry*100]			
Tip	-COOH	$-NH_3$	$-CH_3$	-OH	-COOH	$-NH_3$	-CH3	-OH	-COOH	$-NH_3$	$-CH_3$	-OH
Sample												
Base	156	120	127	85	284	128	321	104	82	6	153	23
Base KB 0.25%	79	83	67	118	126	53	96	140	58	-35	43	19
Base KB 0.5%	127	76	72	179	81	96	88	140	-36	26	22	-22
Base KB 0.75%	105	53	65	142	154	89	86	148	47	66	31	4
Base Elv. 0.5%	318	174	143	166	505	201	244	202	59	16	70	22
Base Elv. 0.75%	269	170	152	165	497	432	283	263	85	154	87	60
Base Elv. 1.5%	225	144	119	117	399	239	182	211	77	66	53	81
Base Elv. 2.0%	232	143	112	121	389	88	211	160	68	-38	89	32
Elv. 0.5% KB 0.25%	180	214	197	114	297	366	310	227	65	71	57	99
Elv. 0.5% KB 0.5%	150	204	190	173	354	317	252	203	135	56	32	17
Elv. 0.5% KB 0.75%	115	203	198	185	445	331	237	218	286	63	20	18
Elv. 0.75% KB 0.25%	255	143	213	138	281	328	310	187	10	129	46	36
Elv. 0.75% KB 0.5%	221	132	171	119	327	348	287	214	48	164	68	80
Elv. 0.75% KB 0.75%	252	127	178	132	309	311	289	206	23	145	62	56
Elv. 1.5% KB 0.25%	220	219	181	116	282	333	284	152	28	52	57	32
Elv. 1.5% KB 0.5%	233	191	178	112	301	164	304	164	29	-14	71	47
Elv. 1.5% KB 0.75%	205	183	159	103	315	273	246	170	53	49	55	66
Elv. 2% KB 0.25%	114	151	151	142	203	204	224	144	78	36	48	1
Elv.2% KB 0.5%	133	148	181	167	442	286	239	179	232	94	32	7
Elv. 2% KB 0.75%	163	135	178	153	275	242	259	164	68	80	46	8

Effect of Kling Beta on moisture damage

Using the –OH tip: The change of cohesion forces of dry and wet samples of 0.5% Elvaloy and the three percentages of KB binder with –OH tip are shown in Figure 5. It is seen that the 0.5% and 0.75% KB are more effective to prevent the moisture damage as they has the least change in cohesion force. So 0.25% KB is not recommended in an environment where the moisture may harm the AC.

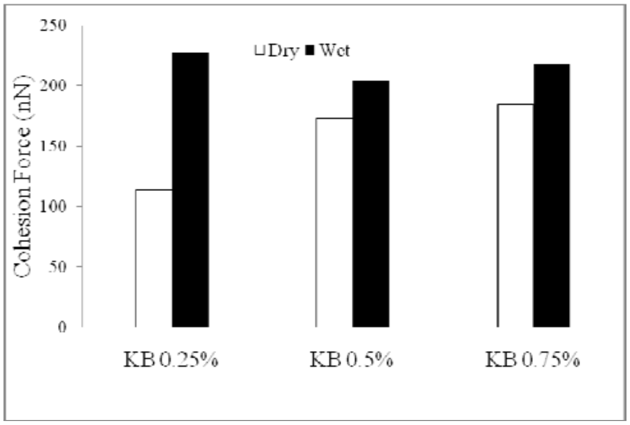


Figure 5. The change of cohesion forces on 0.5% Elvaloy and three percentages of KB with –OH tip

Using the –CH_3 tip: Figure 6 shows the effect of mixing KB on moisture damage. The base binder was modified with three percentages of KB. Here 0.5% KB is seems to be the most effective to prevent the moisture as it has the lowest amount of cohesion gain. The 0.25% KB has the worst performance against moisture damage. The performance of 0.75% KB is in between of 0.25% KB and 0.5% KB.

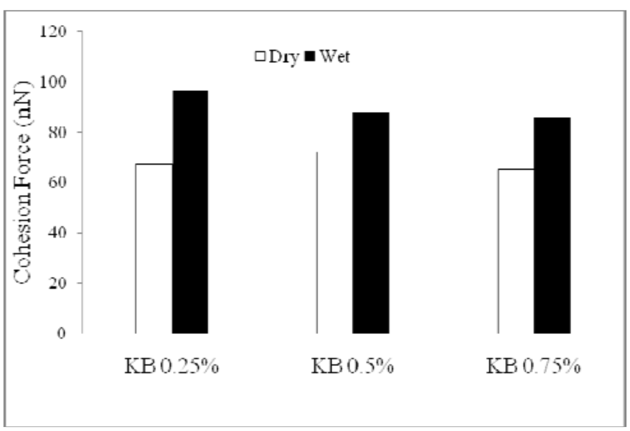


Figure 6. The change of cohesion forces on Base (PG 58-28) and three percentages of KB with – CH_3 tip

Using the –NH_3 tip: Figure 7 shows the cohesion force results when the 0.5% Elvaloy modified binder was tested with the – NH_3 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.

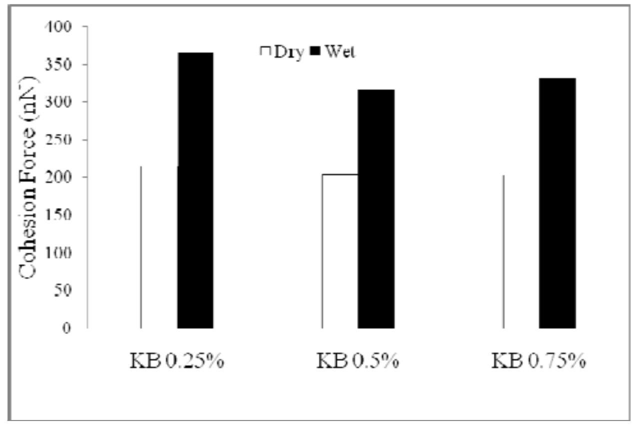


Figure 7. The change of cohesion forces on 0.5% Elvaloy and three percentages of KB with – NH_3 tip

13. CONCLUSIONS

For the first time in asphalt pavement engineering, this study introduces the use of functionalized AFM tips to determine the moisture damage with antistripping agents. The conclusions are following:

- Moisture affects asphalt binder as there is difference between wet and dry samples adhesion.
- Antistripping agent reduces the adhesion that is moisture damage.
- The 0.5% to 0.75% antistripping agent (KB) is the most effective to prevent the moisture damage.
- -COOH functional in asphalt does not have significant effects on moisture damage or adhesion property.

14. ACKNOWLEDGMENT

This project is funded by the National Science Foundation (NSF) through the prestigious CAREER program. NSF grant number: 0644047 and Program: Structural Materials and Mechanics (SMM). Special thanks go to Larry Bank, NSF program director, for visiting our lab Center for High Tech Materials (CHTM) at the University of New Mexico recently. Thanks to Randy Clark and Bob McGinnis of Holly Asphalt Company for his assistance in obtaining the material needed for this study. The authors would like to express sincere gratitude towards Richard Teran of Veeco Instruments.

15. REFERENCES

[1] Shin-C. Huang, 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] R. Tarefder, and A. Zaman, "Nanoscale Evaluation of Moisture Damage in Elastomeric Polymer Modified Asphalts", ***ASCE Journal of Materials in Civil Engineering,*** American Society of Civil Engineers (accepted), 2010.

[3] 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.

[4] B. Ohler, "Cantilever spring constant calibration using laser Doppler vibrometry". **Rev. Sci. Instrum.,** Vol. 78, No. 06370, 2007, pp 1-5.

[5] S. Testa, "Chemical Aspect of Cold-Mix Asphalt Incorporating Contaminated Soil". **Journal of Soil Contamination,** Vol. 4, No. 2, 1995, pp 1-17.

[6] 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.

[7] 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.

[8] 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.