

The Investigation of 'Bee-Structures' in Asphalt Binders

Benjamin McCarron¹

Xiaokong Yu², Mingjiang Tao², Nancy Burnham¹

1 Department of Physics, Worcester Polytechnic Institute

**2 Department of Civil and Environmental Engineering, Worcester Polytechnic
Institute**

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Abstract

Asphalt binders (bitumen) are used heavily in construction and have been found to possess a unique and complex microstructure that contains 'bee-structures'. Past literature suggests these structures are composed of waxy materials, thus they should dissolve at higher temperatures into the rest of the asphalt binder. These structures have been studied with an Atomic Force Microscope (AFM) under changing thermal conditions in order to learn how to make asphalt concrete more recyclable and reduce the occurrence of potholes. Experiments have shown that as temperature increases the height of the bee structures decrease by an average of 32% with a standard deviation of 16. This information was obtained via cross section analysis comparing structures at room temperature and 45 C°.

Acknowledgements

Xiaokong Yu², Mingjiang Tao², Nancy Burnham¹

1 Department of Physics, Worcester Polytechnic Institute

2 Department of Civil and Environmental Engineering, Worcester Polytechnic Institute

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Executive Summary

Asphalt binders, otherwise known as bitumen, are crucial in modern construction. Bitumen has been found to possess a complex microstructure composed of several organic and inorganic compounds. The sheer complexity of bitumen itself has made defining its exact structure difficult. Bitumens from different sources also have different compositions and properties. In 1996, Loeber et al. coined the term 'bee-like structures' to describe a main feature in their studies of bitumen at the nano-scale. Since their discovery, these bee structures have been studied by several groups. Other literature suggests that the structures are composed of a wax, which has been observed to melt at high temperatures.

For this project, an atomic force microscope was used to analyze the microstructure of bitumen. All experiments were performed with cantilevers with a nominal spring constant of ~ 5 N/m and a frequency of ~ 127 KHz, and were performed in intermittent contact mode. Problems with thermal drift were anticipated; thus, initial experiments were performed on a glass slide and a pressed CD sample mounted to a slide via double stick tape in order to analyze the effects increasing temperature during continuous imaging. Graphs of displacement vs. temperature for the glass and pressed CD samples show that despite the difference in thermal expansion coefficients, their thermal drifts were comparable. This suggests that the drift was caused by the machine rather than the individual samples. Future experiments were performed on bitumen and used to compare the thermal drift to that of glass and pressed CD samples. The bitumen had comparable drift to that of both the glass and pressed CD sample, confirming previous conclusions.

Initially, the sample preparation method for the bitumen was to be the solution cast method. Upon lack of results, the heat cast method was chosen. Heat cast samples are thicker and have more structures

than their counterparts. The heat cast samples used in the experiments were made by heating the bitumen in an oven to ~160 C then dropping a small amount onto one side of each slide. The slides were then put back in the oven at an angle such that the bitumen would streak towards the other side. This created an even film that could be imaged. After about two minutes, the slides were removed and cooled for two days to allow the bitumen to settle for imaging.

Once sample preparation had been remedied, experiments began to produce relevant results. Initial experiments showed that bee structures were scattered evenly in bitumen samples in random directions. The average length of these structures was found to be approximately 5 microns. During thermal experiments, images were taken in 5 degree Celsius increments from ambient temperature (approximately 20 degrees Celsius) to the maximum capability of the heating panel (45 degrees Celsius). After each image, there was a rest time of twenty minutes at constant temperature to allow the samples to settle after the heating process.

These experiments were performed on two different binder, AAD and AAE. AAD had a higher wax content than AAE. Consequently, AAD showed more bee structures than the AAE samples which showed no definite structures similar to Loeber's. As the temperature increased, the length, width and height of the bee structures decreased. This was discovered when cross sections were analyzed via the line measure tool.

Future experiments should focus on the difference between waxy and non-waxy bitumen as well as be performed with a heater capable of reaching higher temperatures. Observing the full dissolution of the structures could be an interesting task. Future work could also focus on relating bee structure formation and dissolution to overall asphalt concrete performance.

Introduction

As of 2009, there were roughly four million miles of road in the United States of America alone. Over 90% of these roads are constructed from asphalt concrete. Asphalt concrete is the obvious choice in many cases due to its durability and its versatility. The ease of use also contributes to its popularity. Asphalt can also be recycled fairly well. During the deconstruction phase, the torn up asphalt is combined with virgin materials to make new asphalt. Sustainability is also a big emphasis because infrastructure is expensive no matter what the material.¹

Publicly funded highway programs make up about 65% of the asphalt pavement market and federal spending accounts for about 42%. Most of the funding at the federal level comes from the Highway Trust Fund (HTF) which is financed primarily by the federal gas tax, which is 18.3 cents on the dollar. This tax, however, has not been raised since 1993 whereas inflation has steadily risen. The rise of inflation has reduced the purchasing power of these 18.3 cents by about ninety percent. This has led to substantial pushes in the development of more durable and longer lasting asphalt.

A common problem with today's roads lies in the formation of potholes and cracks in the asphalt. These are often a major inconvenience and repairs are costly to say the least.

“According to the National Surface Transportation Policy and Revenue Study Commission of the U.S. Congress, the annual investment required by all levels of government to simply maintain the nation’s highways, roads, and bridges is now estimated to be \$185 billion per year for the next 50 years. Today, the nation invests \$68 billion.”¹

In order to decrease the required spending, recycling the asphalt has become a major focus. Recycling asphalt keeps it out of landfills as well. This is another benefit to sustainable asphalt.

Today the asphalt industry reuses and recycles roughly 100 million tons of its own products annually. The recycled asphalt is referred to as Reclaimed Asphalt Pavement (RAP) and is incorporated into new pavement. The asphalt cement in the RAP is reactivated when combined with new pavement, becoming the glue that holds it all together.

Asphalt is composed of a binder called bitumen mixed with aggregates (small stones, pebbles, etc.), Bitumen is composed of four components: Saturates, Asphaltenes, Resin, and Aromatics (SARA).² The bitumen only accounts for about 5% of the mixture but provides the asphalt with many of its macro-scale properties (color, hardness, flexibility, etc.), Bitumen is a product derived from crude oil. It is the “bottom of the barrel” component in the refining process. Many studies of bitumen have been performed; however, the exact chemical composition cannot be clearly defined as the bitumen itself is very complex and varies from well to well.³

The studies of bitumen have shown that as the scale of observation is decreased from macro- to micro- to nano- that there are microstructures within this mysterious albeit widely used substance. Loeber *et al.* is credited with the first study of bitumen at the nano- level.² He discovered a strange structure that he referred to as ‘bee-like.’ The structure is composed of several periods of maxima and minima of material within a short span concentrated in an elliptical fashion. These high and low waves are seen as a pattern of light and dark stripes, thus the image of a bee as seen in Figure 1. These structures were discovered using an Atomic Force Microscope (AFM), which is used extensively when studying samples at the micro- and nano- scale of research.

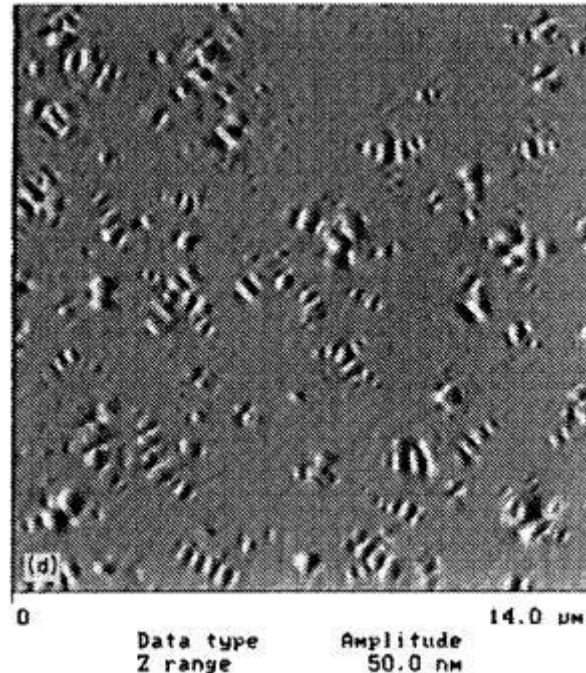


Figure 1: Loeber's bee structures (Black is low, white is high.)²

The experiments will investigate the material properties of bitumen at the nano-scale, mainly the properties of the bee-like structures. The study hopes to answer questions about the evolution and dissolution of these bee-structures as a function of temperature. Pauli *et al.* noted that the structures were dependent on not only the thickness of the sample, but that the structures seemed to 'melt away' with repeated scans. This was attributed to the heat from the laser, implying that the material's melting point was within the temperature range of the laser reflected onto the cantilever. Studies of bitumen have shown that these structures are only prevalent in samples with some wax content and that when wax is added to non-waxy samples the structures appear.

The hypothesis for this study is that the structures *are* composed of wax crystals and as such are prone to melting at easily attainable temperatures. The utilization a heating stage will allow for the increase of the temperature of the sample, which will cause the wax crystals to melt and the structures should disappear. Time permitting; the study would encompass the effect of substrate (glass vs.

aluminum), sample thickness, and environmental factors (e.g., water) on the evolution and dissolution of these bee structures. The evolution and dissolution of the structures may also coincide with the crystallization and melting of wax crystals within the bitumen. The experiments will be performed with an AFM with thermal capabilities in a room with a temperature and humidity sensor. These external sensors will allow for the moderation of the surrounding environment.

Other studies performed on bitumen have proved difficult due to thermal drift within the sample. Bitumen is very sensitive to changes in temperature (high coefficient of thermal expansion). Constant monitoring of the images will allow for changes in the offsets in order to keep track of the microstructures in question. Bitumen is also very viscous and sticky; the sample could very easily contaminate the cantilever tip during the data collection. This contamination can lead to distorted images.

The results could help to define the composition of the structures based on their melting point of the structures and could bridge the knowledge gap between chemistry and the mechanical performance of asphalt. These data could lead to the development of more durable and sustainable asphalt concrete, eliminating potholes and saving the country billions of dollars in road construction and repair.

Following this chapter is the Literature Review, which will summarize related works in order to perform a more comprehensive study. Afterwards, the Methods section will describe processes used throughout the experiments performed. Results and Discussion will be a detailed analysis of the products of the experiments, which will be followed by a Conclusion and Future work section to sum up and describe expansions of the project itself.

Methods

The objective of this research is to investigate the material properties of the bitumen micro-structure classified as a bee structure by Loeber et al.² This is necessary to understand the macro-scale properties these structures have on asphalt. Two types of asphalt binder will be analyzed using an atomic force microscope (AFM). A heating element will be in place in order to observe the effects of temperature on the binders. (See Appendix A)

Sample Preparation

These studies, in the interest of time, will focus on two types of bitumen only, ABD and AAE. Two types are being used because the chemical composition differs between each type. The wax content in each type has been reported to be responsible for the formation of bee-structures.^{4, 5,6,7,8} Studying two types allows for the comparison of obtained results.

Samples will be prepared using a solution cast method as opposed to a heat cast method. The solution cast method allows for multiple samples to be made quickly and does not involve any heating procedures to complicate preparation. The solution cast method does have some disadvantages; after the samples are prepared, they must be left out for a minimum of one week to allow the excess toluene to evaporate. Another disadvantage of this preparation method is that it may affect the chemical bonds within the binder. A detailed explanation of solution cast sample preparation can be seen in Appendix B.

The heat cast method⁹ involves the preparation of pure bitumen on glass slides. Heat cast samples are generally thicker and opaque where solution cast are thinner and transparent. This method was not chosen because the samples are generally too thick to measure effectively and preparation is more complicated. Preparation involves heating the bitumen to 160 degrees Celsius which means that

protective gloves are required. Each sample also requires about half an hour to prepare due to heating and cooling times.

Atomic Force Microscopy

Atomic Force Microscopy (AFM) is used extensively when studying samples at the micro- and nano-level. The AFM uses a tiny silicon cantilever to scan the surface of the sample in a raster pattern. The changes in the height of the sample are detected by a photo-diode which measures the position of a laser beam reflected off of the back of the cantilever arm during the scan. The cantilevers consisted of a macro scale rectangular base, a long, thin arm, and a fine tip. The tips of these cantilevers can have a radius of just a few nanometers; however, most tips on average have a radius of ~100 nm. The components of the AFM can be seen in Figure 2.

There are several different scanning modes that one may use during an AFM experiment: contact mode, intermittent contact mode, and non-contact mode are the principal ones. Contact mode is fairly intuitive; the cantilever tip stays in contact with the sample throughout the entire scan. This leads to results that are fairly easy to interpret, however, this tip-sample interaction can lead to contamination and wear of the tip which may produce misleading AFM images. The next mode, intermittent contact mode, relies on the vibration of the cantilever at resonance. This decreases the wear and contamination of the tip if used properly and is commonly used with viscous or adhesive samples. These results are harder to interpret and much less intuitive than those produced by contact mode. Non-contact mode is used when tip-sample contact is unwanted. This is often the case with samples that will bind to the tip and immediately cause contamination or breakage.

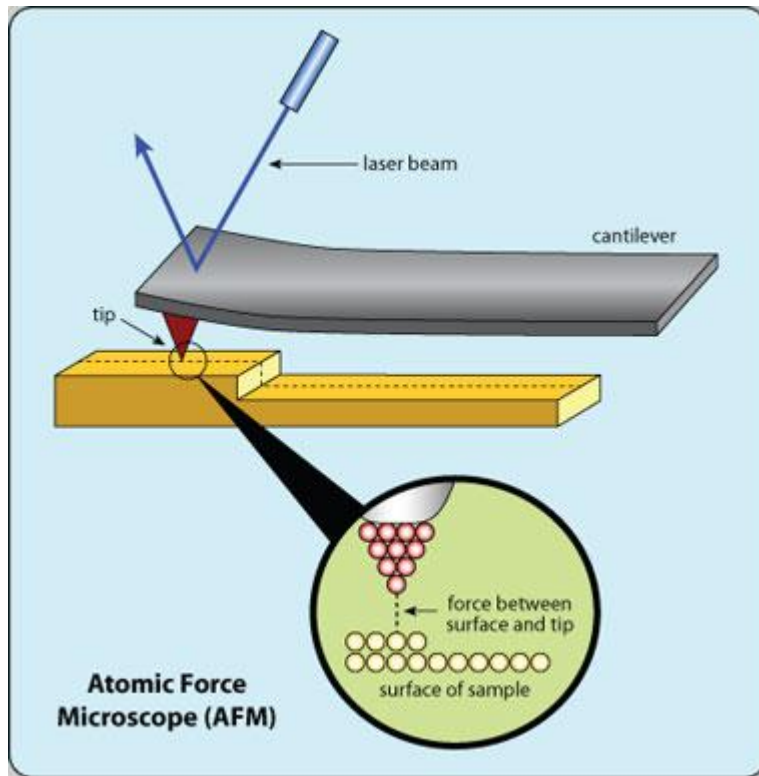


Figure 2: A breakdown of the components of the Atomic Force Microscope 13

During the experiments, the use of the Asylum AFM Petri Dish heater and the Environmental controller are critical. A detailed description of the usage of the Petri Dish Holder and Heater can be found in Appendix A. These allow the user to heat the sample and monitor temperature changes. Throughout the imaging process, the temperature will be ramped up at one (1) degree per minute, a typical value. Every 3 degrees, an image will be taken once the temperature has settled. This will continue up from ambient temperature (~22° Celsius) to 45°C (the maximum range of the heating element). These images will be used to measure the drift in the sample as well as the evolution and dissolution of the structures.

Thermal Drift

Every material has a coefficient of thermal expansion which denotes how that material expands or contracts in the presence of dynamic thermal conditions. The coefficient for bitumen is on the order

of magnitude of $10^{-4}/^{\circ}\text{C}$. For most other materials, this coefficient is on the order of $10^{-6}/^{\circ}\text{C}$. Bitumen's is 100 times greater, thus, bitumen is very sensitive to temperature changes. This challenge may be overcome by very slow adjustment of the temperature during experiments and adjusting the AFM's offsets. Taking images at step intervals of temperature will allow the bitumen to settle such that drift is not occurring during each 20 minute image.

A material with a comparable coefficient to bitumen's is double stick tape. Thus, a sample of a pressed CD was mounted on an aluminum slide with double stick tape in the hopes of observing this drift on a familiar sample. (Appendix C) This experiment led to the conclusions that samples tend to drift in a south westerly direction (Figure 1 and 2 in Appendix C) and at a constant rate with temperature. (Figure 3 and 4 of Appendix C) It is recommended to start with a wide scan range during temperature ramping experiments to ensure the focus of the experiment does not leave the image.

Literature Review

Bitumen is one of the many by-products of crude oil refinement. After a lengthy process through several heating and cooling stages and distillation columns, bitumen is left behind. In Figure 3 it is clear to see that the crude oil is put through a furnace and heated to about 300 C before going through an atmospheric distillation column where the first set of separation occurs. The heavier elements go through a second furnace and into a vacuum distillation column where the heaviest elements, namely the bitumens, are left at the bottom. It is the thickest, most complex part of the crude oil. (Figure 1)

Bitumen has a variety of uses in construction such as roofing and pavement manufacturing.

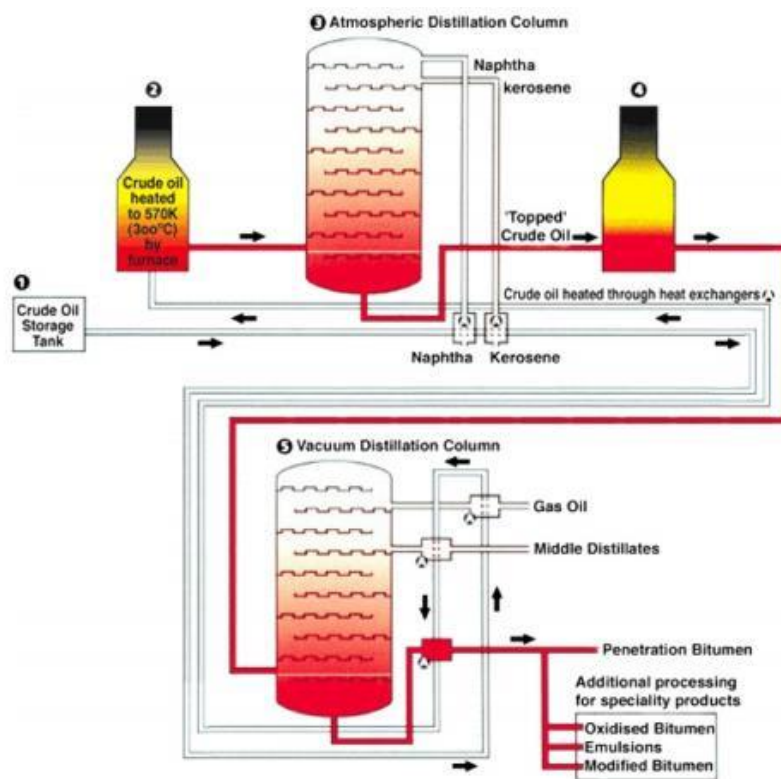


Figure 3: The distillation of bitumen from crude oil to bitumen collection ¹⁰

Until recently, bitumen was only studied at a macro scale level. With the advent of Atomic Force Microscopy (AFM) came a technique to study this substance at a molecular and nano-scale level. Loeber

was one of the first to put this substance under this new microscope and observe the microstructure.² Since then, several other studies have been performed by teams across the world.^{4,5,7}

These teams have studied bitumen in the hope that information about this substance gathered at the nano-scale level will help to create better roads. In Figure 4 there is a breakdown of how macro-scale asphalt behaves under certain environmental conditions as well as with time. At the molecular level, historical studies have shown that there are at least hundreds of thousands of unique molecular species that exist within any particular asphalt.¹¹ These individual species can be split into polar and non-polar compounds with varying degrees of each. Both polar and non-polar compounds and/or groups affect the macro-scale asphalt in different ways.

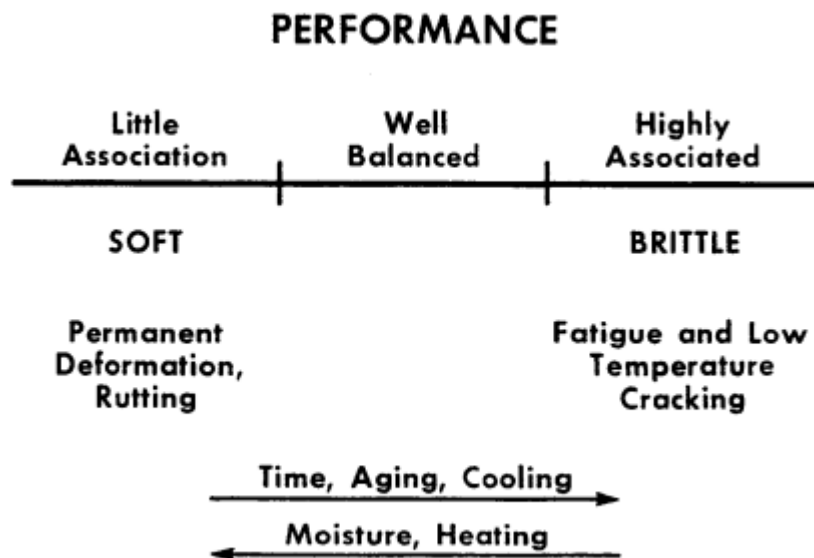


Figure 4: Performance of asphalt based on environmental conditions¹¹

Polarity is a very major contributor to the performance characteristics of the asphalt. Polar materials tend to associate strongly into a matrix which is dispersed in less polar and non-polar materials where the exact chemical formula is less important than the total assembly of the matrix. Polar compounds provide structure and stiffness while excessive polar compounds lead to stiff asphalt

which is in turn brittle and tends to crack. Non-polar compounds provide the asphalt with some viscosity, but too many can lead to rutting in the pavement.

One problem with studying bitumen comes from its chemical complexity. Bitumen has been studied in micro scale under a plethora of conditions and with several variables; teams have observed how bitumen acts in extreme cold ⁶ and under wet conditions ⁸ to test for loss of adhesion between aggregate and bitumen; teams have altered wax content and changed sample thickness. In each case, the scientists observed the bitumen in order to determine how these experiments provided insight into the behavior of bitumen at the macro level.

One paper studied the effect of water damage to asphalt ⁹. They took AFM images of wet and dry bitumen as seen in Figure 5. The surface became much rougher when water was introduced. This means that the water had a negative effect on the cohesion of the bitumen particles to one another.

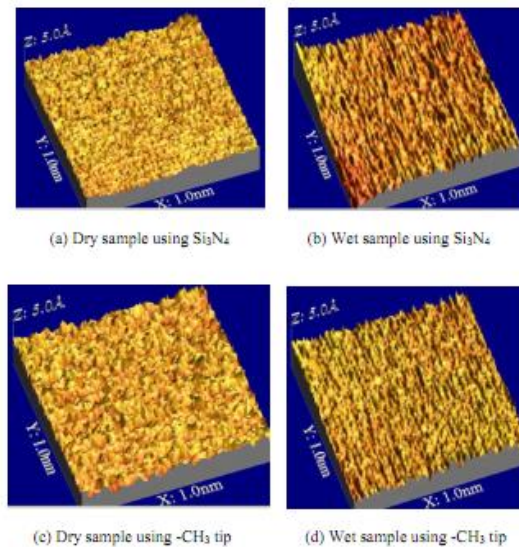


Figure 5: Surface images of asphalt samples (1% SB) ⁹

Bitumens from different sources not only have different names and properties, but different compositions as well. This has led to studies being performed on several types of bitumen at once in

order to compare and contrast results. This makes experiments more complex and tedious as each must be repeated for every sample. This is a blessing and a curse in that certain bitumens perform better under different conditions in terms of asphalt performance. Roads in colder climates and roads with warmer climates are made from different bitumen in order to increase longevity and decrease maintenance costs.

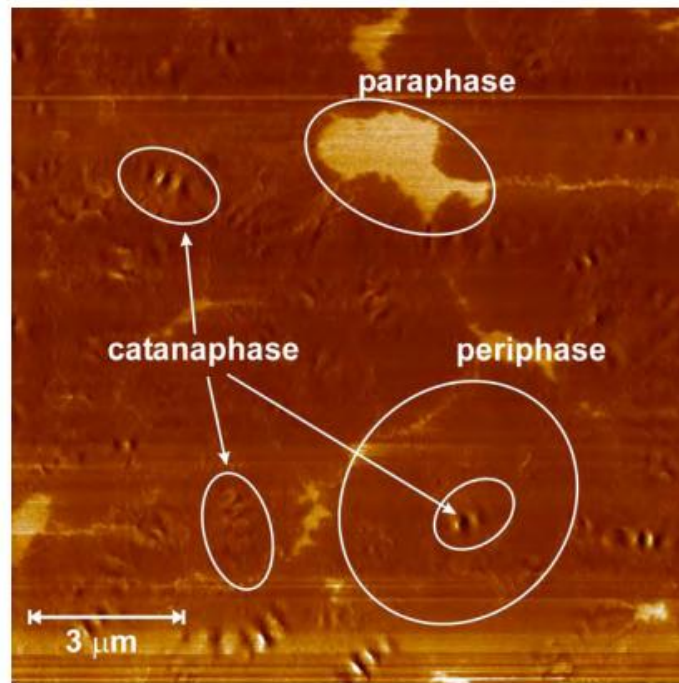


Figure 6: Catana, Peri- and Para-phases of bitumen via Phase Detection Microscopy ⁶

Researchers have attempted to simplify bitumen classification through fractionation. Bitumen has been broken into its fractions: Saturates, Aromatics, Resins, and Asphaltenes (SARA). Each of these groups can be observed in the separate phases of bitumen via Phase Detection Microscopy (PDM) as seen in Figure 6. PDM measures the phase shift of the oscillating cantilever relative to the driving signal. This phase shift can be correlated with specific material properties that effect the tip/sample interaction. The phase shift can be used to differentiate areas on a sample with such differing properties as friction, adhesion, and visco-elasticity. ¹²

The phases are arranged by polarity⁶. The polar saturates form the catana phase which most papers refer to as the 'bee-structure,' coined by Loeber et al. in his paper. This phase is immediately surrounded by the peri-phase composed of the aromatics and resins. These are more non-polar than the saturates, but more polar than the asphaltenes which form the para-phase, furthest away from the bee-structures. These claims are supported by the glass transition temperatures of each fraction compared to the phase images at decreasing temperatures. A fourth phase, the salphase, is observed which, even at very low temperatures, does not freeze. The salphase is generally found in concentrated points within the para-phase of the bitumen. (Figure 7)

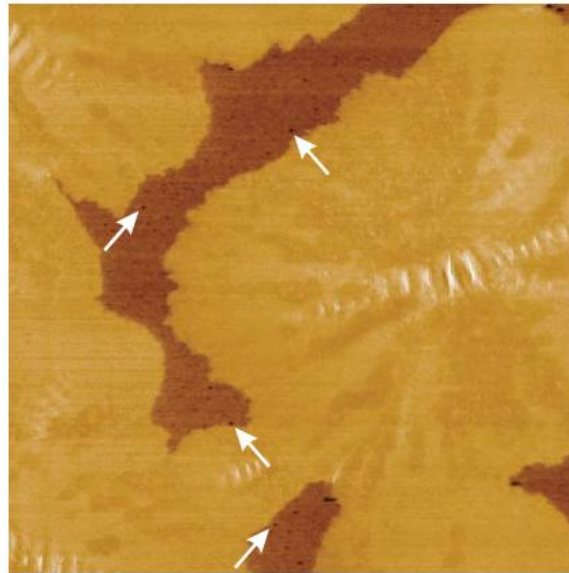


Figure 7: A 15 x 15 micron image of AAN bitumen. The salphase can be seen as the concentrated dark spots in the para-phase. The color contrast covers a variation in phase angle of ~100 degrees.⁶

Bitumen, when imaged with an AFM, has a complex and curious set of microstructures, the main example being the bee structure or catana phase. Several studies have investigated this structure, starting with Loeber et al. in 1996. Loeber coined the term 'bee-like structures' to describe these bunched up group of mass sporadically arranged throughout his bitumen samples (Figure 6). What causes these structures has been investigated in multiple instances. One particular paper written by

Pauli et al. attributes these bee structures to crystallized wax content within the bitumen (Figure 7). They performed several experiments, testing the effect of sample thickness as well as wax content within a sample. Pauli et al. found that thinner samples mean fewer, smaller structures and that as temperature increased, the structures tended to dissolve away.

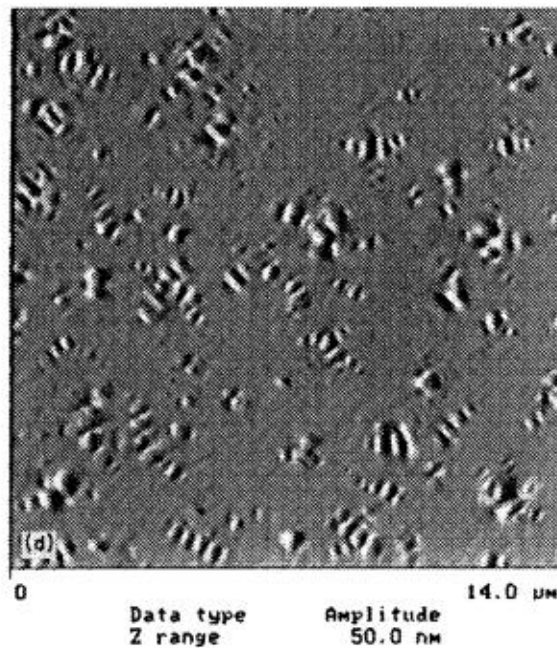


Figure 8: One of Loeber's first images of bitumen microstructure and the bee structures

During their own investigation of the bee structures, one group measured the relative stiffness of several areas in and around the structure. They found that there were four distinct zones within the vicinity. Each zone had a different stiffness and can be seen in Figures 6 and 7. The goal of these experiments was to test the effect of 'bitumen-scale' qualities and their effect on 'mastic scale' qualities, the next level up.

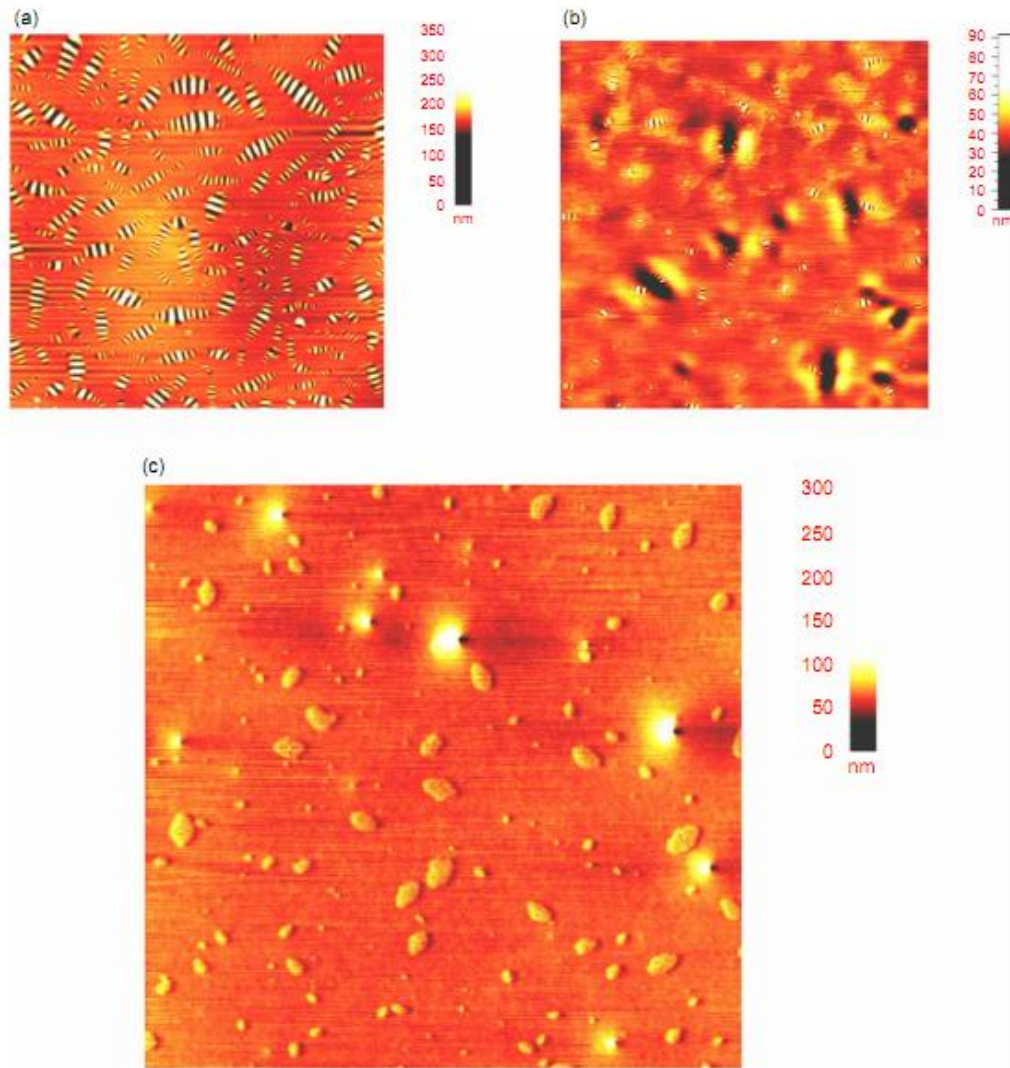


Figure 9: AFM topography images of bitumen films of varying thickness. (a) 1 micron, (b) .1 micron, and (c) .01 micron ⁴

The actual content of the bee structures has been investigated as well. At this point, the most recent studies ^{4,6,7,8,12} seem to agree that they are composed of wax. It was found that samples with no wax content produced no bee structures and that samples which previously showed no structures exhibited them on the addition of wax content (Figure 10). Also, less wax content meant smaller bee structures.

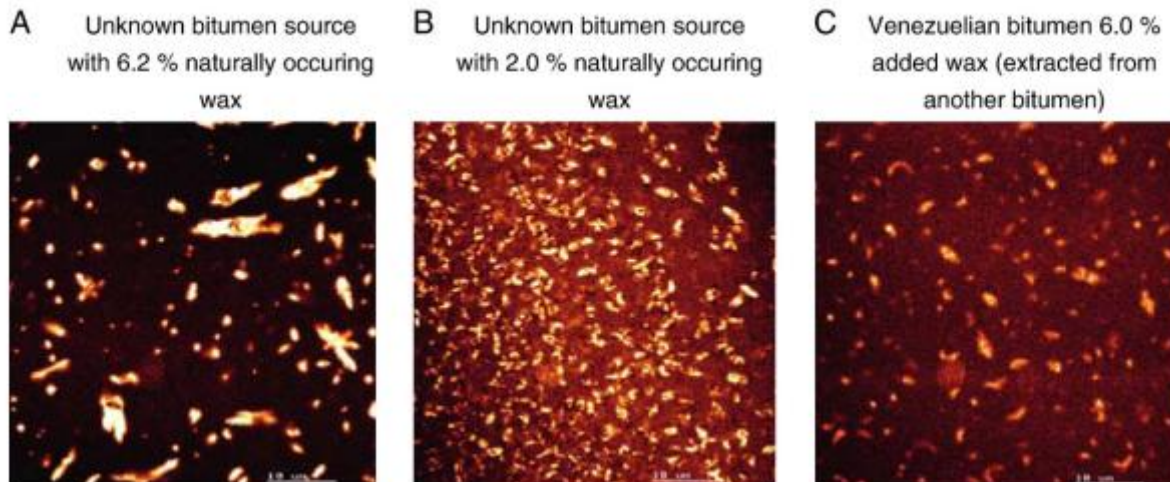


Figure 10: Various geometries of wax crystals inside bitumen as observed by Confocal Laser-Scanning Microscopy. The scale marks 10 microns.¹⁰

One paper goes over several experiments performed in order to discern the content of the bee structures as well as their behavior under different thermal conditions as well as over time.^[7] Xiaohu Lu et al. examine nine different bitumens, eight waxy, one non-waxy. They found that non-waxy bitumen displays no structure or crystals using Confocal Laser-Scanning Microscopy (CLSM). Waxy bitumens from different crude origins display a large variation of structures. They vary from tiny needles, elongated needles, flakes, and even crescent shaped structures. The morphology of the wax crystals is highly dependent on crystallization temperature as well as temperature history. Wax which has been isolated from waxy bitumen and mixed into non-waxy bitumen displays similar morphology as the wax in the original bitumen. Bitumen wax usually melts at lower temperatures than 60 C° although in one case a temperature of 80 C° was needed until complete melting of the wax.

Moraes et al. studied bitumen at high temperatures up to its melting point (~170 C°).⁸ They verified that the bee structures disappeared in higher temperatures around 57 C°. They also found that after cooling down from 170 C° the bee structures began to reform at this same temperature. As bitumen cooled to 56 C from heating, the structures could be seen to reform. Immediately the reformation was evident as seen in Figure 11. This temperature was found to be the melting point of

wax and thus lends itself to the hypothesis that the structures are made from crystallized wax within the bitumen. In each separate image, the insets are a phase image of the assigned bee structure and are of the same area. The bee, as probed at high temperature presents a softer phase in each case.

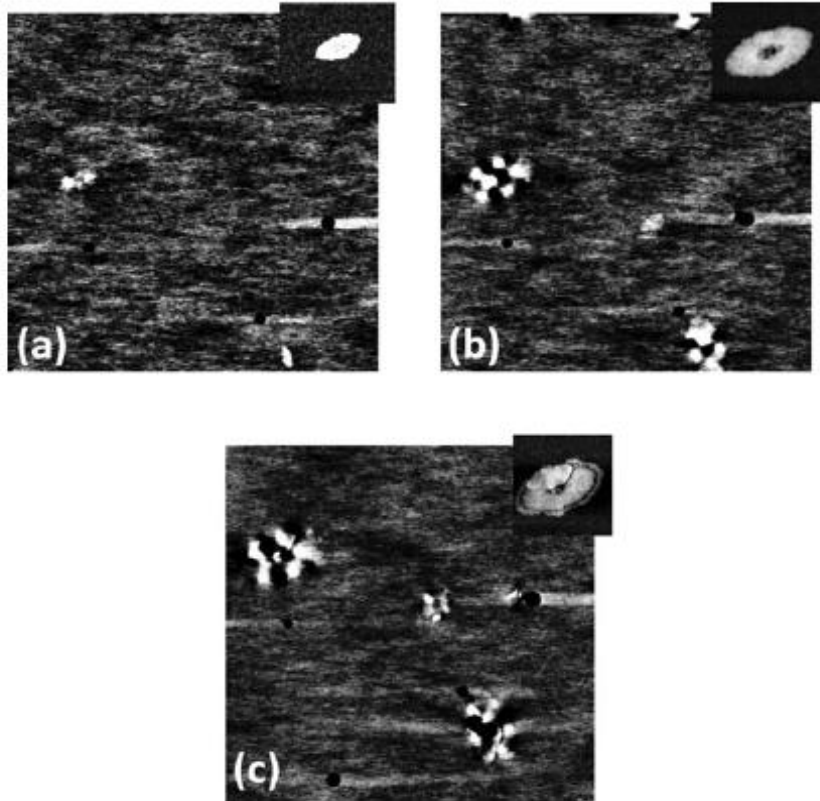


Figure 11: The reformation of bee structures as the sample is cooled from 57 C to 56 C. (a) is at $t=0$, (b) is at 44 mins after reaching 56 C and (c) is at 95 mins. The insets are phase images of the same bee structure.¹²

Studies of bitumen's aging process have also been performed. As stated in Figure 4, aging has an effect on asphalt properties. Thus, artificially aged bitumen was studied by H.L. Zhang et al.¹² They also added a clay compound called organo-montmorillonite (OMMT) to the bitumen in an amount of 3% by weight and aged the modified bitumen as well. The aging process was performed in two methods, a UV lamp and the Thin Film Oven Test (TFOT). In each case, bitumen was imaged pre-modification via OMMT and after. Both phase and topography images were taken to observe effects of modification and aging combined. H.L. Zhang et al. found that the addition of OMMT decreased the size of bee-structures.

Additionally, after the TFOT, the unmodified bitumen showed little contrast between phases, in contrast of Figure 6 where each phase is distinct. In order to verify that wax is indeed responsible for bee structure formation, H.L. Zhang et al. separated the waxy portion, the asphaltenes, from the maltenes (un-waxy) and imaged both. Only the bitumen with the asphaltenes showed bee-structures. (Figure 12)

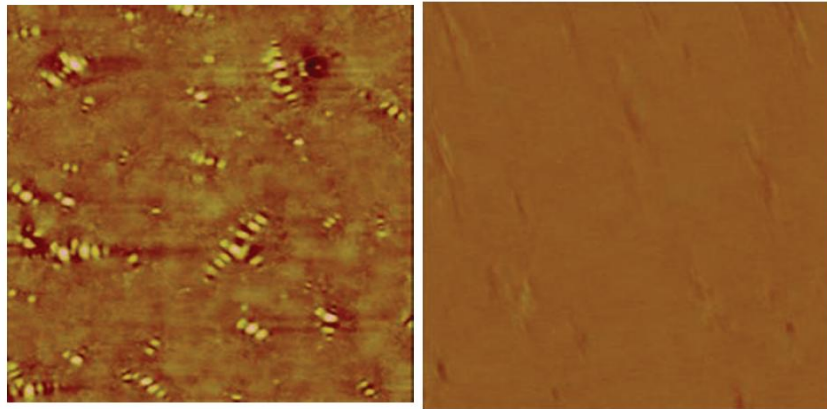


Figure 12: Bitumen with asphaltenes (left) and without (right) ¹²

Each of the studies of bitumen suggests that wax is indeed responsible for the formation of bee structures. During our studies of the material, we expect to find that the structures are tending to change shape as the temperature is increased. Unfortunately, our heating element cannot reach the temperatures found to melt the wax. We hope to find that different bitumen wax melts at lower temperatures. Force curve acquisition could also suggest that the bee structures are softer at higher temperature.

Results and Discussion

Initial experiments on the asphalt binder were performed on solution cast samples. These samples proved to be too thin and did not show any bee structures, thus the solution cast method was abandoned and replaced by the heat cast method for the rest of the studies.

Heat cast samples were adopted because they provided more structures to observe. Samples were prepared by dropping hot binder on the clean glass slides and letting the binder flow down the slide to form an even coat. Two samples were made of each binder imaged.

Experiments were performed from ~20 to 45 degrees Celsius. Images were taken at five degree intervals and in each case the sample was allowed to settle for twenty minutes at constant temperature. Topography, error signal, and phase images were all simultaneously acquired in intermittent contact mode on binders AAE and AAD.

AAE Results

AAE was known to have a very small wax content compared to AAD. Images of AAE showed no bee structures (Figure 13) and instead showed a series of fractal-looking canyons. Previous study of asphalt binders in literature showed few images similar to those found in binder AAE. The low wax content was most likely responsible for the lack of bee structures found.

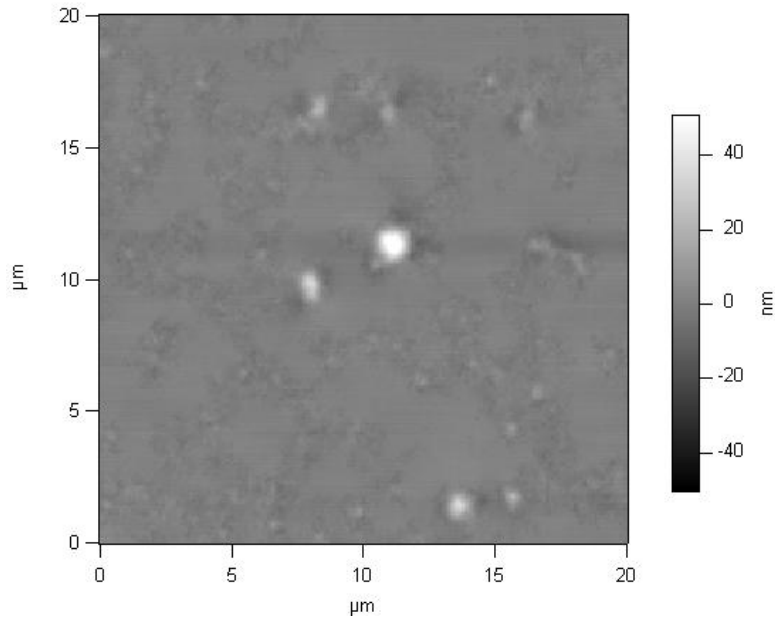
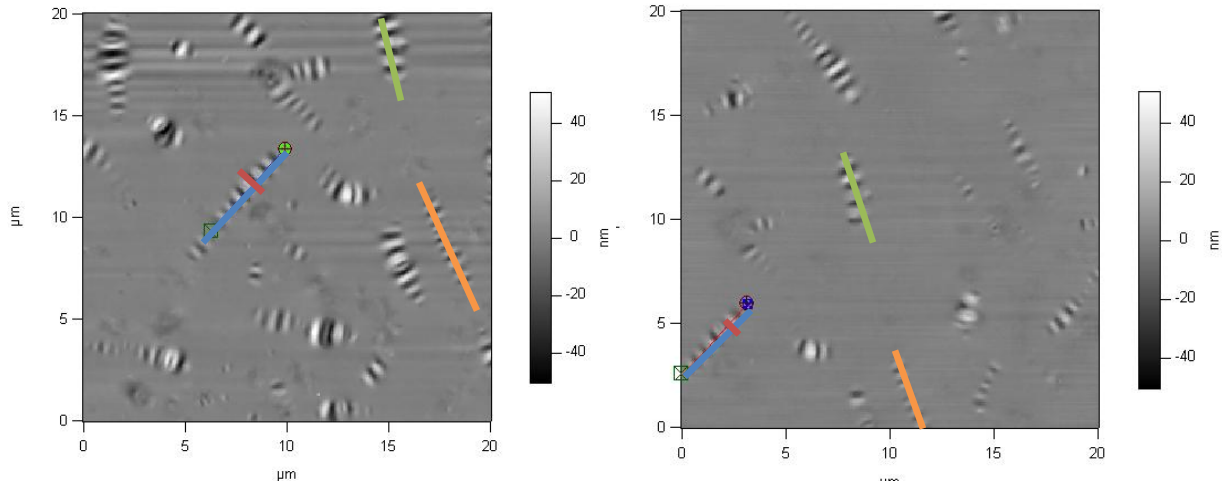


Figure 13: Image of low wax binder AAE at ambient temperature

AAD Results

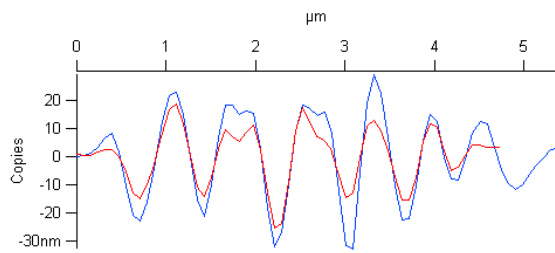
As the temperature of the sample increased the size of each bee structure imaged decreased. This is seen in Figure 14. Cross sections were taken of several structures at ambient temperature and 45 degrees. In each case, the structures can be viewed as waves. The amplitude of each structure decreased with temperature while the wavelength remained fairly constant. This trend leads to the conclusion that temperature has a great effect on the binder, even within a small range (only about 25 degrees Celsius). In several cases, the measured structures drifted such that they were partially out of the image in either in the first or second image; however, the cross sections that could be compared still agreed with data from fully visible structures.



Before: 20 degrees

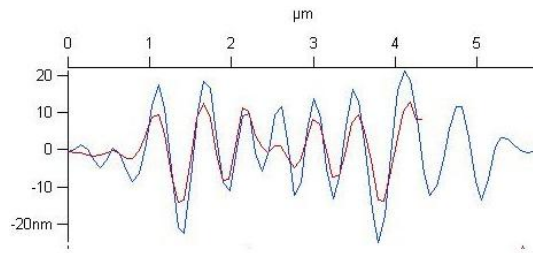
After: 45 Degrees

Blue Line:



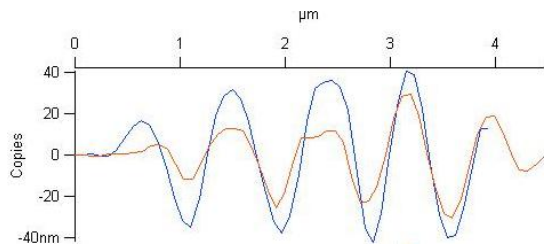
Blue: 20 degree, Red: 45 degrees

Orange Line:



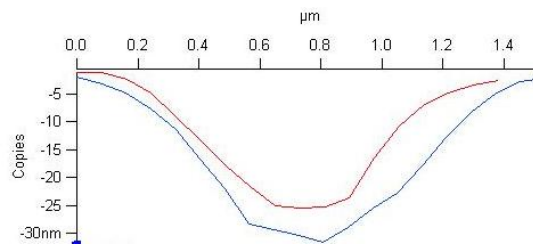
Blue: 20 degrees, Red: 45 degrees

Green Line:



Blue: 20 degrees, Orange: 45 degrees

Red Line:



Blue 20 degrees, Red: 45 degrees

Figure 14: Comparison of cross sections of several bee structures. Each colored line on the original images is represented by a separate figure below. The average decrease in amplitude was calculated to be $38\% \pm 16$.

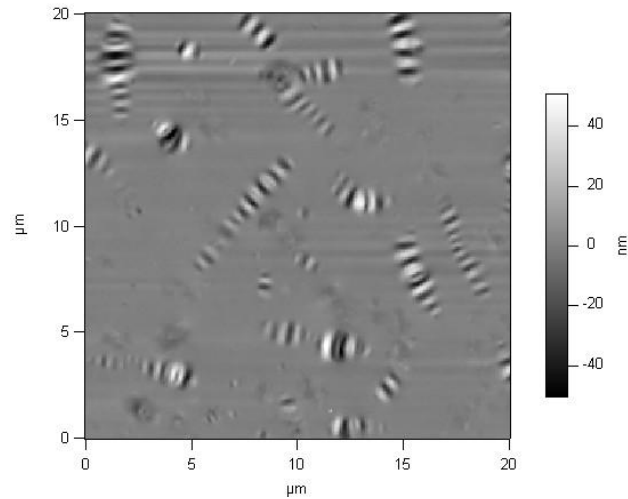


Figure 15: Image of higher wax content binder AAD at ambient temperature (Approx. 23 degrees Celsius)

The width of the trough of one structure was measured for quantitative purposes and found to decrease from approximately 1.5 microns to 1.3 microns. The amplitude of this same trough was seen to decrease from 30 nanometers to approximately 24 nanometers. This is a 20% decrease over an interval of 25 degrees Celsius. In some cases, this decrease was as much as 50 percent from maximum amplitude. The average decrease in amplitude was calculated to be 32% with a standard deviation of 16. Most changes were from 25 to 50%. There are several comparisons between cross sections at 20 and 45 degrees in Figure 14. Previous studies have shown that the bee structures dissolving away at a specific temperature and then evolving once the temperature was decreased again. These data show that the dissolving of the structures is a gradual process and that it doesn't just begin at the melting/freezing point.

In order to quickly compare the before and after images in an overall manner, Fourier transform techniques were used. This method compares the contrasts of the two images and breaks them down into frequencies. This is much faster than the cross section by cross section method and gives insight

into the big picture. Fourier transform images were taken of a region contained within both the ambient and 45 degree images of the AAD data. Comparisons of these two Fourier transforms can be seen in Figure 17. The FFT image of the initial image shows a brighter center with a larger radius which means that the high frequencies are more present in the image. The larger radius of the dark half circle shows that the image also has more low frequency wave patterns.

Discussion

In the scientific literature reviewed before these experiments, several papers discussed the reason that these bee structures formed. Many attributed the structures to wax crystallization within the binder itself. Binder AAE (1.2%) has much lower wax content than binder AAD (2.5%). As seen in the figures, AAD showed bee structures and AAE did not though in each case the samples were prepared at the same time and under the same conditions.

AAD Images had many structures present as seen in Figures 2 and 3. Each topography image has a height range of 100 nanometers and is 20 x 20 microns. As was found in both the glass and CD samples, thermal drift occurred. The drift amount over the full range of heating was approximately 8 microns, very similar to that of the glass and pressed CD sample. This confirms that the sample's coefficient of thermal expansion is not responsible for drifting during AFM imaging.

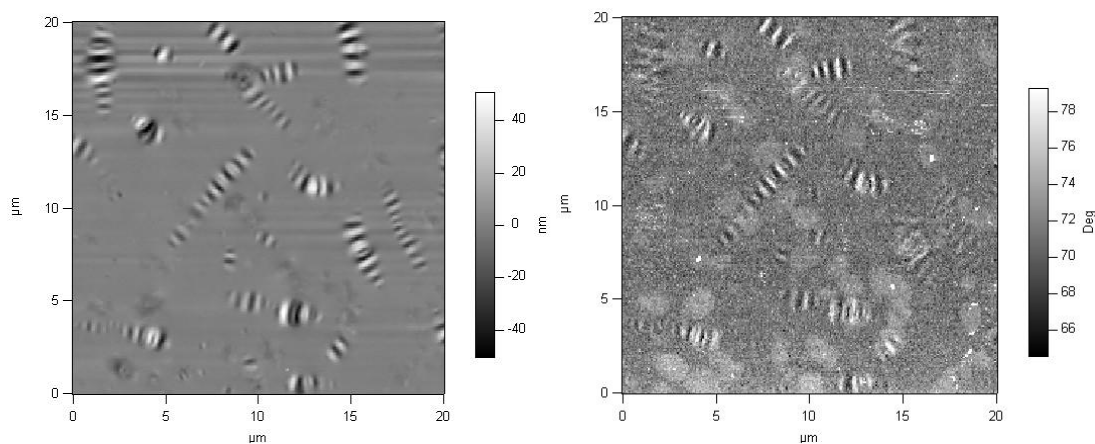
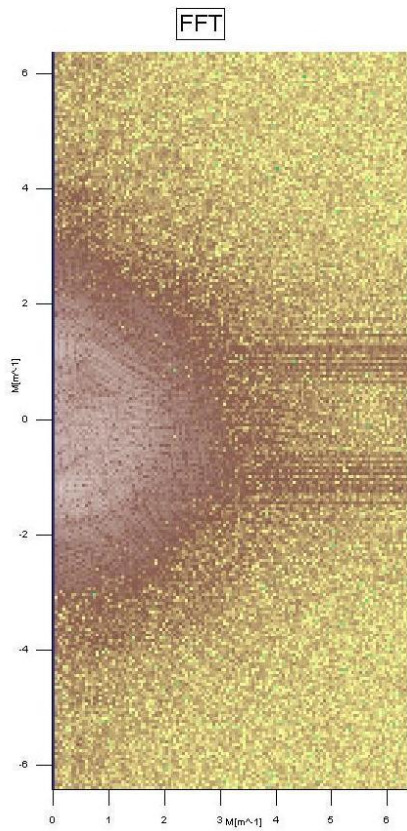
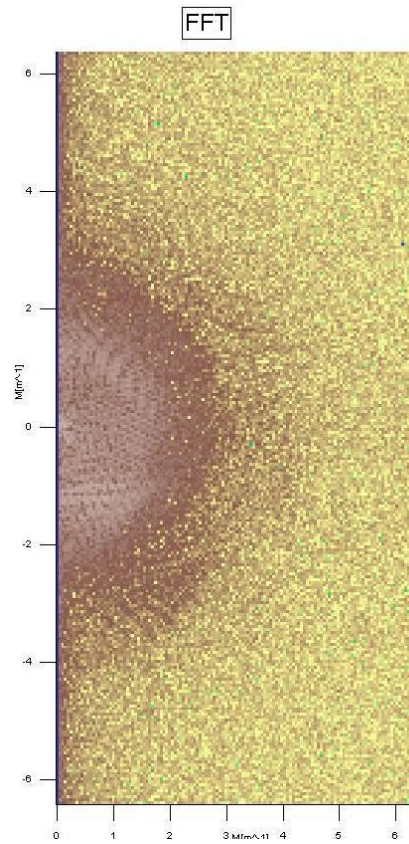


Figure 16: Phase image (right) of higher wax content binder AAD at ambient temperature (Approx. 23 degrees Celcius)



Temperature: 20 degrees Celcius



Temperature: 45 degrees Celcius

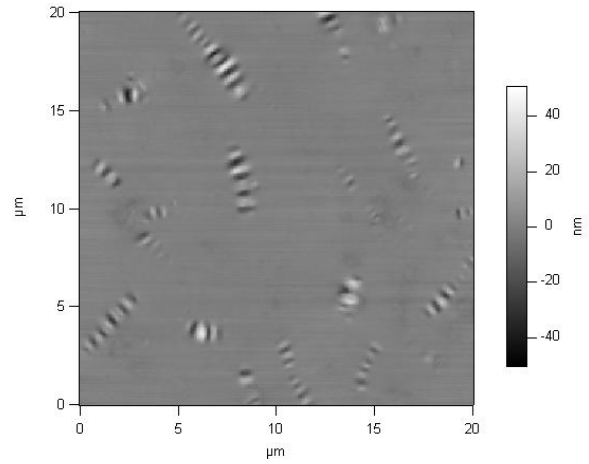
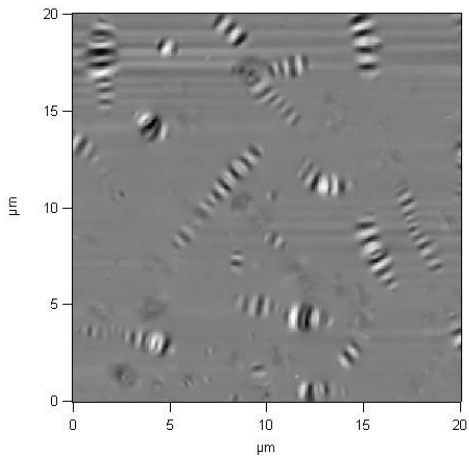


Figure 17: Fast Fourier Transform (FFT) images of AAD at 20 and 45 degrees celcius. The left the side image is rougher and has taller bee structures thus the FFT has a brighter center and the radius is larger.

Phase images were widely discussed in the literature, thus during imaging, phase images were collected. Those taken were found to consist of the same distinct phases found in previous papers. The bee structure phase surrounded by a darker matrix phase with lighter, discrete phases dispersed throughout. Each of these phases was found in a range of only about 12 degrees, yet they are very distinct. An example of a phase image obtained during AAD imaging can be seen in Figure 16.

As for the changes in the structure of the bees, there are several possible reasons. Increasing temperature could cause the wax crystals to melt back into the matrix phases of the bitumen. This melting would decrease the size and shape of the structures uniformly and take place from the outside in towards the center. These structures were also imaged several times. This means that the cantilever tip could be responsible by shaving off the tops of the structures with each pass. Bitumen is a viscous material and thus is susceptible to changing shape. The tip of the cantilever could also wear down during imaging. This would decrease the resolution of the images with each pass and make features seem shallow and more blunt compared to the initial images taken with a sharper tip. This distortion is common among AFM images.

Future Work

This project can serve as a starting point for several other studies. One obvious addition would be studying and comparing the effects of temperature on other binders (ABD, AAB, etc.). Each binder is different in terms of composition though they are all considered bitumen.

Experiments could be performed on non-waxy bitumen to see if structures are present. Afterwards, adding wax artificially could cause the evolution of bee structures. Comparing artificially and naturally waxy bitumen under changing environmental conditions could lead to information that would

affect the choice of bitumen during construction and answer the question of wax's benefits. These experiments could also be done with different waxes and different wax percentages.

The main focus of all of these experiments is to increase the sustainability and performance of asphalt concrete on the macro-scale. Analyzing the different bitumens and then making macro scale asphalt samples with the same bitumen to compare properties could answer questions about importance of wax content and bee structure formation.

Conclusions

From the data presented, one may conclude that temperature indeed has an effect on size and shape of bee structures. As the temperature increased, the size of the bee structures decreased by an average of 38% with a standard deviation of 16 and in some cases the shape of the structures changed. FFT images confirm this as high temperature images showed a smaller radius in the image and thus a 'smoother' image with less sin and cosine components. Since AAE had less wax than the AAD, one may conclude that wax could indeed be confirmed as responsible for bee structure formation

Appendix A

Petri Dish Heater

Installation

****Note**** Credited to Rebecca Gaddis, PH '12

XY Hysteresis Measurement

Before Changing Plate: Measure XY scanner hysteresis (piezos and mechanical assembly)

1. Open the **Test Panel**
 - a. **Note:** This is done on the surface without a tip or sample and scanner head off of the stage
 - b. Click the **Programming** drop down menu then **Load Test Procedures**
 - c. Select the **Testing** drop down menu then **Test Panel**
2. On the **3D Test Panel**, see Fig. 1 select the **Calibration** tab and enter the following parameters.
 - a. In the Channel field: X-axis
 - b. In the Action field: Measure Hysteresis.
 - c. Frequency: 1:0 Hz
 - d. Cycles: 50
 - i. The Piezo will cycle 50 times through three voltage ranges; 160 V, 10 V, and 1V
3. Then click Start button
 - a. A graph of LVDT sensor signal vs. piezo drive voltage will appear.
 - b. Wait for LVDT range to stabilize (50 cycles).
4. Then click Start again (done twice to ensure accurate results).
5. Repeat the procedure for Y-axis (channel).
 - a. The X and Y hysteresis values should be as follows: $\leq 5\%$ for 160 V, $\leq 4\%$ for 10 V and $\leq 3\%$ for 1 V.
 - b. Typical the Y channel values are greater than X.

c. Record value to compare to the values obtained after heater is installed.



Figure 1: 3D Test Panel

Changing the Plate

1. The scanning head should have been removed in the previous section. If it is not, remove it now.
2. Unplug the connector and remove the spring controlling the stage (y-translation).
3. Using a .050 inch allen wrench remove (4) screws and washers holding the sample plate. The screws are located at the back of the stage see Fig. 2a.
4. Clean water shield and exposed stage with cotton swab and alcohol as needed see Fig. 2b.
5. Turn stage upside down such that the screw holes are facing you.
 - a. Position petri dish holder/heater beneath scanner and align holes.
 - b. Start all 4 screws then tighten in a diagonal pattern.
 - c. Be careful not to over tighten.
 - d. Re-position stage with new plate, see Fig 2c.
6. Retest X and Y scanner hysteresis.
 - a. If the three hysteresis values are not similar to the previous values then the plate is most likely

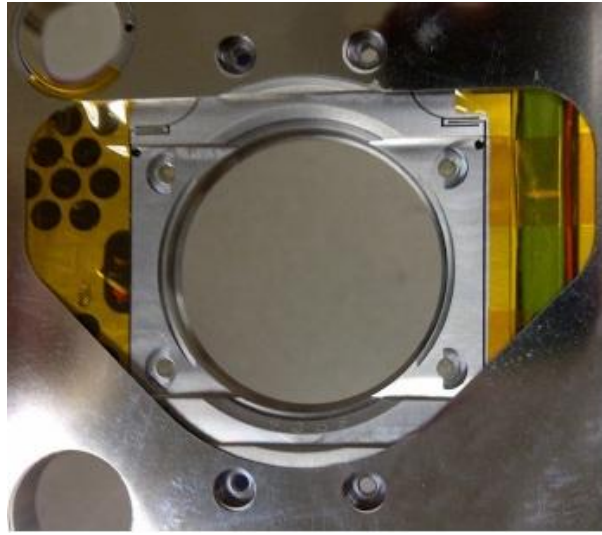
touching scanner.

b. Re-position plate and re-do hysteresis.

7. After hysteresis testing is complete place scanner back onto stage and re-attach y translation spring and plug the connector back into stage.

8. Plug petri dish heater plate cable into the environmental controller (EV controller).

9. Plug the 25x25p interconnect cable from the environmental controller to the MFP3D controller.



(a) Bottom of Stage



(b) Exposed Stage



(c) Petri Dish Heater

Using the Petri Dish Heater

1. Ensure the EV (Environmental) controller is on
2. Open a new template in MFP3D
 - a. Heater panel window should automatically appear see Fig. 2.
 - b. If it does not see page 13 of the Petri Dish Holder and Heater manual, found on the AFM Lab computer desktop under "manuals" and at www.AsylumResearch.com.
3. Turn on the heater by selecting "on" for the following:
 - a. Feedback
 - b. Heater
4. Enter desired parameter values
 - a. Target temperature: this is typically 37°C for mammalian cells.
 - b. Note the following phenomenon and adjust parameters as needed:
 - i. The temperature sensor is located inside the sample plate therefore the measured temperature is lower than the fluid/slide temperature.
 - ii. The difference between these temperatures is dependent on how well heat is coupled into bottom of the glass slide or petri dish.
 - c. Ramp temperature: how quickly the sample should reach target temperature. I.e. for a biological sample it may be 6°C/min is typical.
5. Allow ten minutes between adjusting the target temperature and measuring or imaging. It takes at least this long for the temperature to stabilize.
6. Display the Temp vs. Time Graph.
 - a. Click on More located next to Display.
 - b. Click a couple of times to bring up both axes.
 - i. The temperature is on the left.

- ii. The heater output is on the right.
 - c. During initial heating monitor the heater output to ensure that it doesn't reach maximum.
 - i. The heater output shouldn't exceed 66% when heating to 45°C.
7. NOTE: The key to successful live cell imaging is to minimize the time that the dish or slide of cells is "sitting" on the heater plate without being imaged. It is important to have the AFM completely setup and "ready to go" once the cells are placed on the sample plate. This is due to the fluid the cells are in drying from the heater plate and the rate at which the cells die.
8. Begin capturing the Temperature data by clicking on the "More" button next to Display.
9. While the fluid temperature is stabilizing, align the laser on the back of the cantilever. Zero the detection. You will notice that the detection will continue to drift until the fluid temperature is stable. During this period you can also tune the cantilever if you will be imaging in AC mode.
10. Follow standard fluid imaging procedures outlined in the MFP-3D manual (Chapters 8 and 9, AC Mode and Contact Mode Imaging in Liquid).

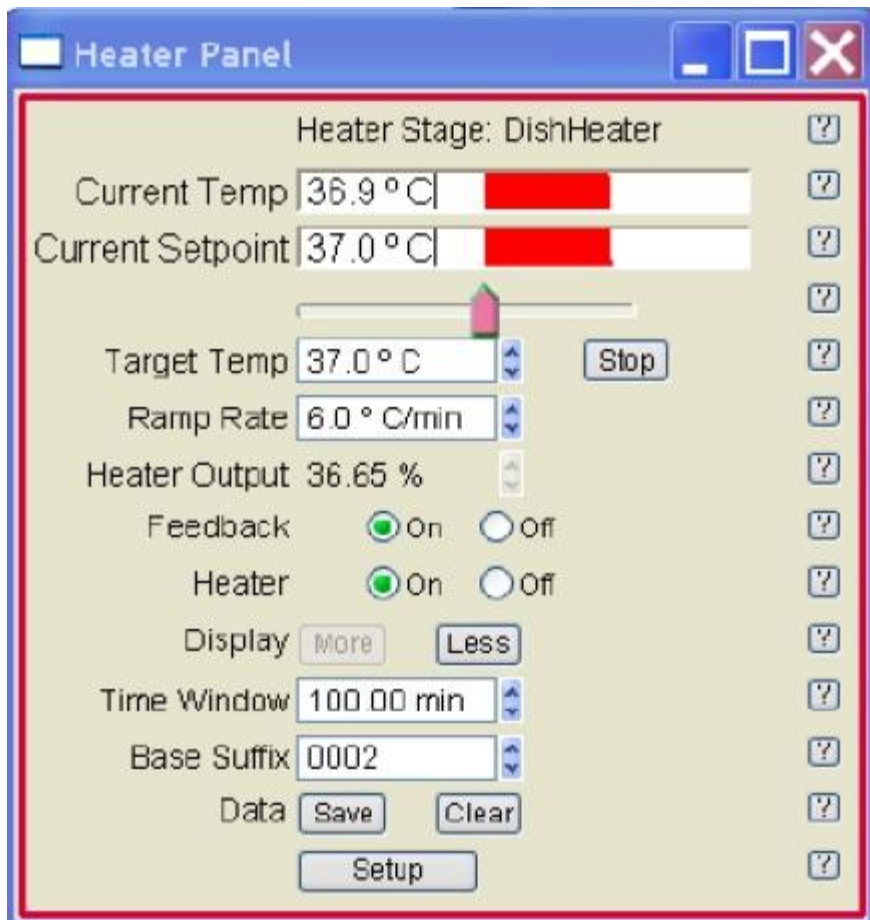


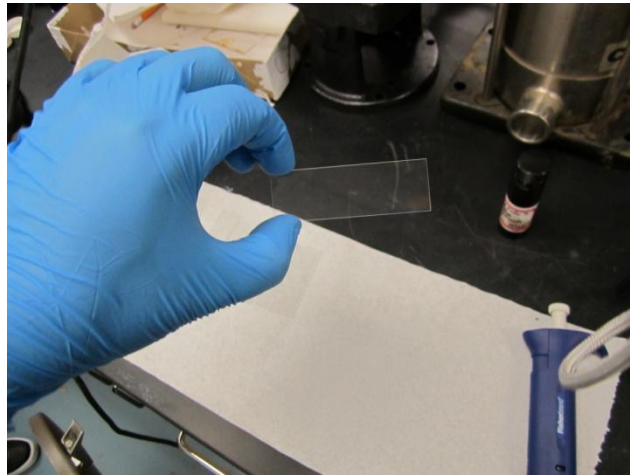
Figure 3: Heater Panel Window

Appendix B

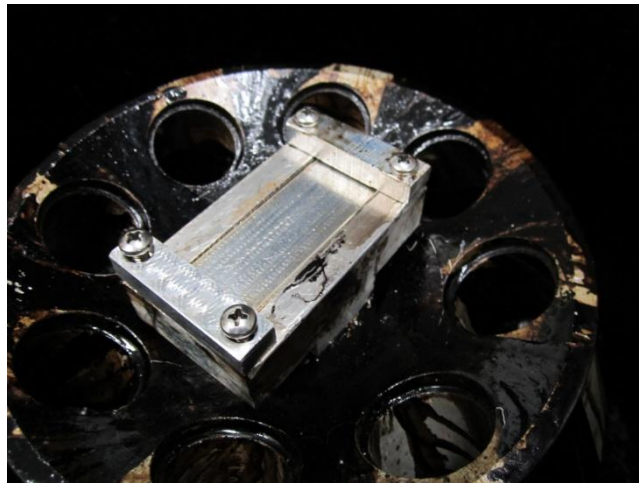
Solution Cast Sample Preparation

The purpose of this appendix is to provide step by step instructions for solution cast sample preparation of asphalt binder.

1. Clean slides with acetone to eliminate dust artifacts. Acetone evaporates quickly so it will not interfere with sample



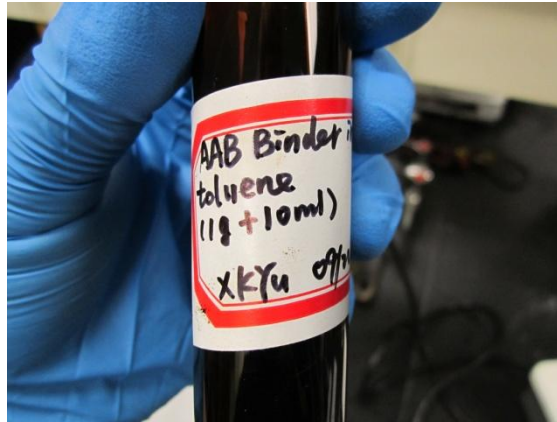
2. Place slide into centrifuge mechanism and tighten screws.



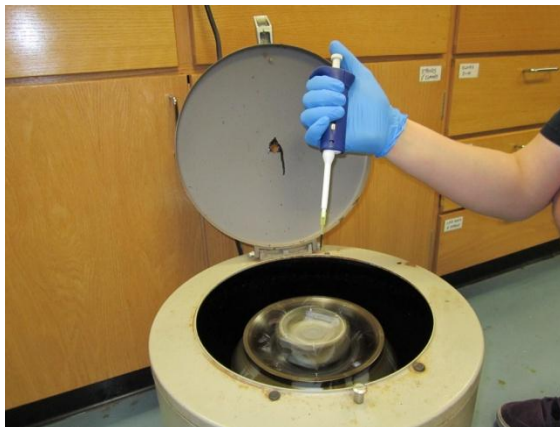
3. Set the micro-pipette to 40 micro liters. The yellow tips are suitable for this volume.



4. Use the micro-pipette to draw in 40 micro liters of the bitumen-toluene solution



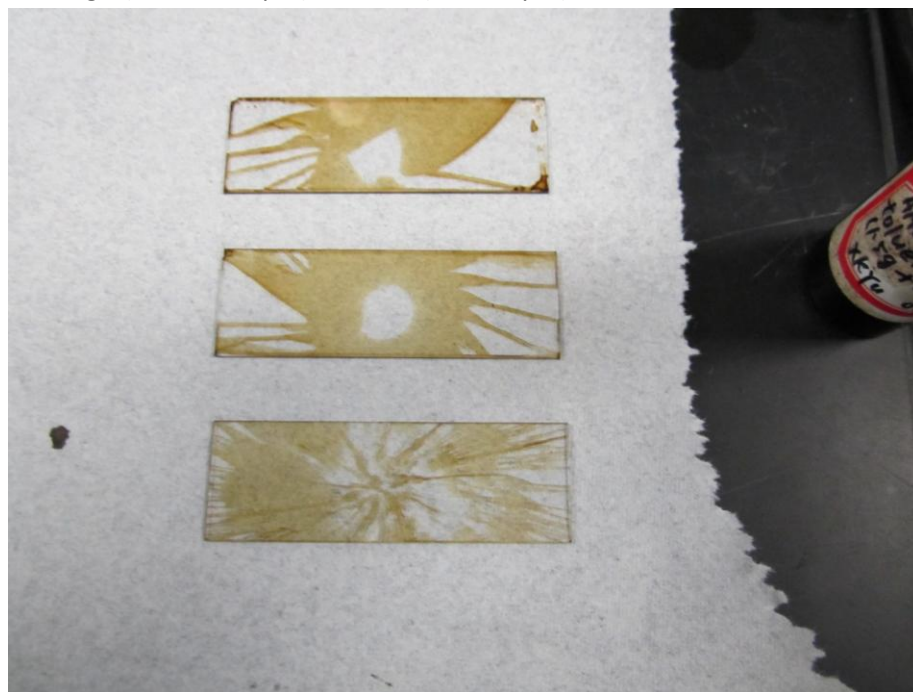
5. Start the centrifuge between ~400 and ~600 RPM



6. Once the centrifuge is spinning at a constant rate, drop the entire solution onto the slide off center at once to ensure even coverage. Leaving a hole in the middle allows for thickness measurements



Examples of samples created under different speed conditions top to bottom: Too slow (Under 300 rpm), on target(400-1000 rpm), too fast (1000+ rpm)



Now these samples must sit for a week so the extra toluene can evaporate. They must be covered so that dust and other contaminants do not ruin them.

Appendix C

Drift Data

Figure 1 represents the drift of a particular dust particle on a glass slide during constant temperature increase of $.5^{\circ}\text{C}/\text{min}$. The data points are at equally spaced intervals of temperature between 24.2 and 44.8°C . Both the y- and x-axis are in microns.

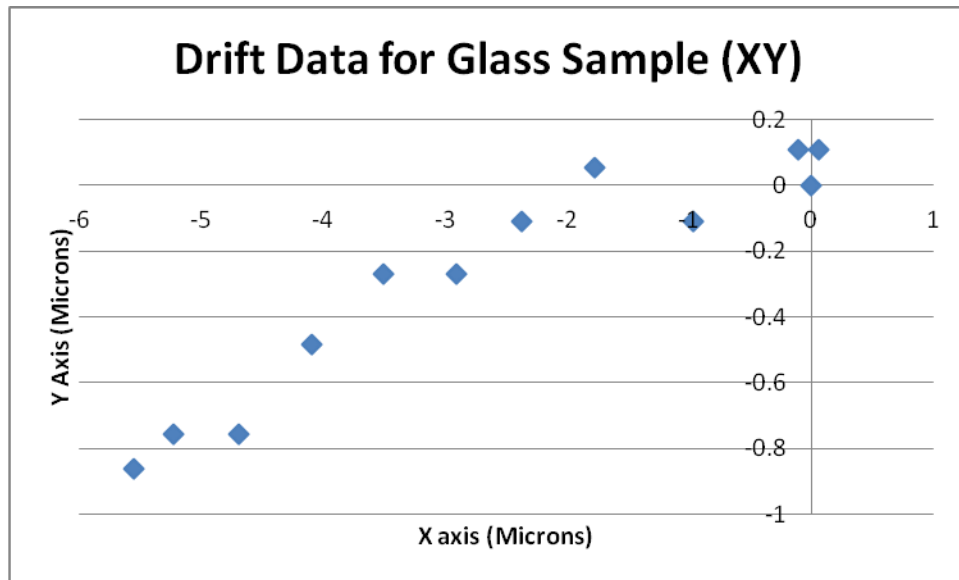


Figure 1: Drift data for a glass sample

Figure 2 represents the drift of a particular bit on a pressed CD sample during constant temperature increase of $.5^{\circ}\text{C}/\text{min}$. The data points are at equally spaced intervals of temperature between 24.2 and 44.8°C . The y- and x-axis are in microns.

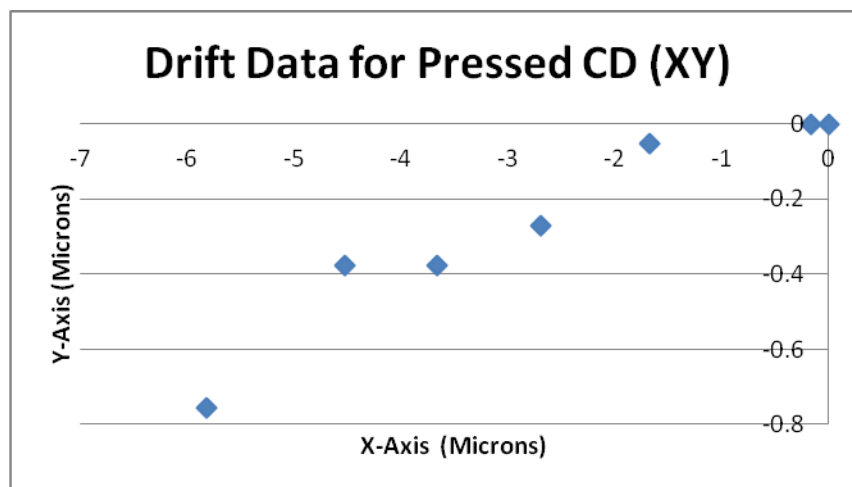


Figure 2: Drift data for a pressed CD sample

Figure 3 represents the radial distance of the particle from the initial point as a function of temperature on a glass sample. The y axis is in degrees Celsius, the x-axis is in microns.

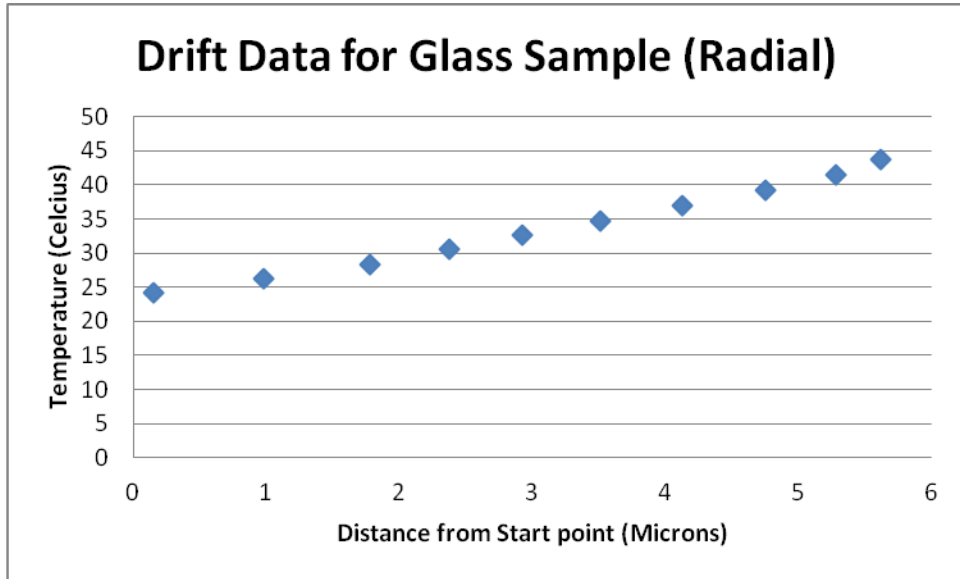


Figure 3: Radial distance vs. Temperature on a glass sample

Figure 4 is represents the radial distance of the bit from the initial point as a function of temperature on a pressed CD sample. The y-axis is in degrees Celsius and the x-axis is in microns.

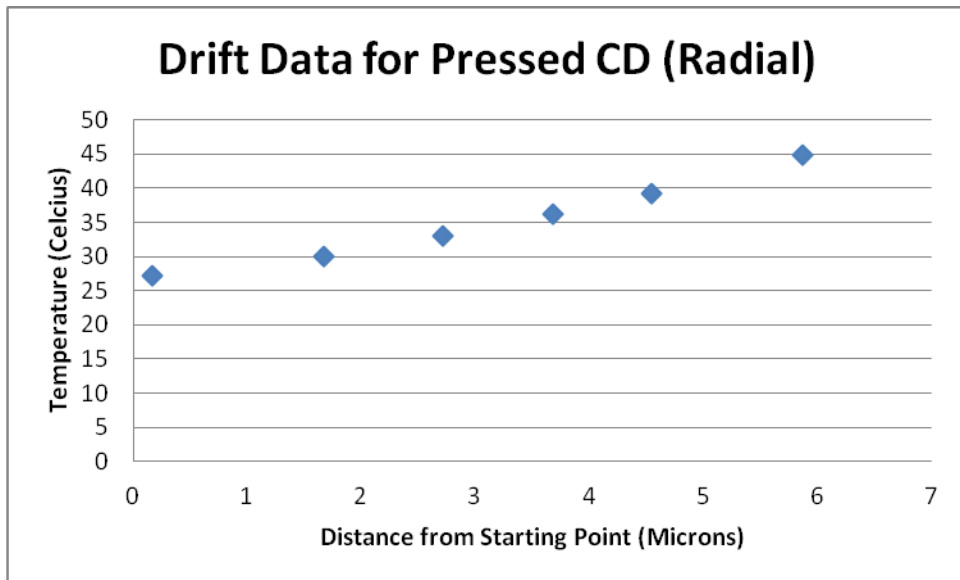


Figure 4: Radial distance vs. Temperature on a pressed CD sample

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