MECHANICAL TESTS ON EPOXY RESIN
NANOSCALE MODULUS MEASUREMENT AND LONG TERM CREEP BEHAVIOR

By

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To my family
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>4</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>7</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>10</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>11</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>1 INTRODUCTION</td>
<td>13</td>
</tr>
<tr>
<td>Overview</td>
<td>13</td>
</tr>
<tr>
<td>Nano-scale Modulus Measurement</td>
<td>13</td>
</tr>
<tr>
<td>The Requirements and Problems for Nano-scale Materials Characterization</td>
<td>13</td>
</tr>
<tr>
<td>Our Solution for nano-scale Modulus Characterization</td>
<td>14</td>
</tr>
<tr>
<td>Long Term Creep Prediction</td>
<td>15</td>
</tr>
<tr>
<td>2 BACKGROUND OF ATOMIC FORCE MICROSCOPE</td>
<td>16</td>
</tr>
<tr>
<td>Operation Principles of AFM</td>
<td>16</td>
</tr>
<tr>
<td>Contact Mode AFM</td>
<td>16</td>
</tr>
<tr>
<td>Dynamic AFM</td>
<td>17</td>
</tr>
<tr>
<td>Force Measurement</td>
<td>19</td>
</tr>
<tr>
<td>Contact Mode</td>
<td>19</td>
</tr>
<tr>
<td>Dynamic Mode</td>
<td>20</td>
</tr>
<tr>
<td>Dual Stability of the Oscillation State in AM AFM</td>
<td>24</td>
</tr>
<tr>
<td>Contact Mechanics</td>
<td>25</td>
</tr>
<tr>
<td>AM AFM Force Measurement for Modulus Mapping and More</td>
<td>27</td>
</tr>
<tr>
<td>3 THE THEORY OF THE FORCE MEASUREMENT METHOD USING AM AFM</td>
<td>31</td>
</tr>
<tr>
<td>Overview</td>
<td>31</td>
</tr>
<tr>
<td>Theory</td>
<td>32</td>
</tr>
<tr>
<td>Existing Background</td>
<td>32</td>
</tr>
<tr>
<td>Multi-region Chebyshev Expansion</td>
<td>35</td>
</tr>
<tr>
<td>Determine the Positions That Separate the Interactions into Different Regions</td>
<td>38</td>
</tr>
<tr>
<td>Numeric Results</td>
<td>39</td>
</tr>
<tr>
<td>DMT Model</td>
<td>39</td>
</tr>
<tr>
<td>Modified JKR Model</td>
<td>40</td>
</tr>
<tr>
<td>Experiments on Polymer Surfaces</td>
<td>42</td>
</tr>
<tr>
<td>Discussion</td>
<td>45</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>2-1</td>
<td>Schematic of a contact mode AFM</td>
</tr>
<tr>
<td>2-2</td>
<td>A typical height vs. cantilever deflection plot</td>
</tr>
<tr>
<td>2-3</td>
<td>Schematic that showing the dynamic AFM tip motion</td>
</tr>
<tr>
<td>2-4</td>
<td>Jump in the ADP curve</td>
</tr>
<tr>
<td>2-5</td>
<td>The Adhesion map</td>
</tr>
<tr>
<td>2-6</td>
<td>Load vs indentation plot</td>
</tr>
<tr>
<td>3-1</td>
<td>The y value for the DMT model</td>
</tr>
<tr>
<td>3-2</td>
<td>The derivative of the y value for the DMT model</td>
</tr>
<tr>
<td>3-3</td>
<td>The DMT model and the reconstructed $Feven (z)$</td>
</tr>
<tr>
<td>3-4</td>
<td>The modified JKR model and their average $Feven (z)$</td>
</tr>
<tr>
<td>3-5</td>
<td>The y value of the modified JKR model</td>
</tr>
<tr>
<td>3-6</td>
<td>The derivative of the y value of the modified JKR model</td>
</tr>
<tr>
<td>3-7</td>
<td>The $Feven (z)$ of the modified JKR model and the reconstructed forces</td>
</tr>
<tr>
<td>3-8</td>
<td>An example of the APD curve on a PS surface</td>
</tr>
<tr>
<td>3-9</td>
<td>The y value for the PS surface calculated from the APD in Figure 3-8</td>
</tr>
<tr>
<td>3-10</td>
<td>The derivative of the y value from Figure 3-9</td>
</tr>
<tr>
<td>3-11</td>
<td>The reconstructed $Feven (z)$ and the hybrid fit for modulus calculation</td>
</tr>
<tr>
<td>3-12</td>
<td>AFM height image showing the 25 grid spots on the PMMA surface</td>
</tr>
<tr>
<td>3-13</td>
<td>25 reconstructed $Feven (z)$ curves overlayed on top of each other</td>
</tr>
<tr>
<td>4-1</td>
<td>Raw amplitude and phase data on fresh cleaved silicon wafer surface</td>
</tr>
<tr>
<td>4-2</td>
<td>Y value calculated from raw data for the reconstruction</td>
</tr>
<tr>
<td>4-3</td>
<td>The derivative of y value</td>
</tr>
<tr>
<td>4-4</td>
<td>The fitting of Chebyshev expansions to the y value</td>
</tr>
</tbody>
</table>
The reconstructed interaction force.......................................................... 73
The individual data points of the reconstructed interaction force.............. 74
Setpoint vs. tip sample distance.................................................................. 75
Setpoint vs. phase........................................................................................ 75
The reconstructed force if the whole data set was used ......................... 77
The overlaid f₀ vs A curves showing the stable windows for ADP curve ...... 78
F₀ vs A plot with four time the free amplitude.......................................... 79
ADP curve trapped in the attractive region, f=f₀+50Hz.............................. 79
Jump from attractive to repulsive region, f=f₀......................................... 80
Jump suppressed, f=f₀-50hz, but phase is noisy...................................... 80
If driving frequency is too low, jump still will happen, f=f₀-100hz............. 80
Higher driving amplitude f=f₀-50Hz.......................................................... 81
Tapping mode AFM height and phase image of Kraton thin film.............. 81
The noise level at different test conditions. .............................................. 82
The two regions of the reconstructed interaction forces......................... 82
The DMT fit to the repulsive region .......................................................... 83
The height and phase image of the PS PMMA blend............................... 84
The overlaid reconstructed force on both PS and PMMA regions............. 85
The MD fit to the repulsive region ............................................................. 86
The load transfer mechanism of an adhesive anchor............................... 99
An example of time temperature superposition ..................................... 100
An example of time stress superposition................................................ 100
The environmental chamber for the long term creep test....................... 101
The test frame setup for the long term creep test................................... 101
The DMA test results for adhesive A......................................................... 102
<table>
<thead>
<tr>
<th>Page</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-7</td>
<td>The DMA test results for adhesive B ................................................. 102</td>
</tr>
<tr>
<td>5-8</td>
<td>The long term strain over time of adhesive A ....................................... 103</td>
</tr>
<tr>
<td>5-9</td>
<td>The long term strain over time of adhesive B ....................................... 104</td>
</tr>
<tr>
<td>5-10</td>
<td>The compliance over time for adhesive A at different load level ............... 105</td>
</tr>
<tr>
<td>5-11</td>
<td>The compliance over time for adhesive B at different load level ............... 106</td>
</tr>
<tr>
<td>5-12</td>
<td>The compliance over time from DSR test of adhesive A ............................ 106</td>
</tr>
<tr>
<td>5-13</td>
<td>The shifted master compliance curve for adhesive A ............................... 107</td>
</tr>
<tr>
<td>5-14</td>
<td>The comparison between prediction and long term test of adhesive A .......... 107</td>
</tr>
<tr>
<td>5-15</td>
<td>The comparison of the prediction of adhesive A with more cure ............... 108</td>
</tr>
<tr>
<td>5-16</td>
<td>The compliance from DSR test of adhesive B at different temperature ....... 108</td>
</tr>
<tr>
<td>5-17</td>
<td>The shifted master compliance curve for adhesive B ............................... 109</td>
</tr>
<tr>
<td>5-18</td>
<td>The comparison between prediction and long term test of adhesive B .......... 109</td>
</tr>
<tr>
<td>5-19</td>
<td>The compliance over time for DSR test of adhesive B at different stresses . 110</td>
</tr>
<tr>
<td>5-20</td>
<td>The shifted compliance curve at different stress for adhesive B .............. 111</td>
</tr>
<tr>
<td>5-21</td>
<td>The shifted factor as a function of compliance from short term creep tests . 112</td>
</tr>
<tr>
<td>5-22</td>
<td>The shifted factor as a function of compliance from long term creep tests .... 113</td>
</tr>
<tr>
<td>5-23</td>
<td>The shifted factor and its linear fit .................................................. 114</td>
</tr>
<tr>
<td>5-24</td>
<td>The difference in stress vs. the slope of the fit .................................. 115</td>
</tr>
</tbody>
</table>
LIST OF ABBREVIATIONS

AM                Amplitude Modulation
AFM               Atomic Force Microscopy
APD               amplitude-phase-distance curve obtained during a cantilever height ramp in tapping mode (AM) AFM
DMT               Derjaguin-Muller-Toporov model of elastic contact
DSR               dynamic shear rheometer
JKR               Johnson-Kendall-Roberts model of elastic contact
FM                the frequency modulation
MW                molecular weight
PS                polystyrene
PMMA              Poly(methyl methacrylate)
UHV               Ultra High Vacuum
WLF               Williams-Landel-Ferry empirical equation for to time–temperature superposition.
With the advancement of nanotechnology, the characterization of materials at the nano-scale has become a challenging yet important task. Amplitude Modulation (AM) Atomic Force Microscopy (AFM) is one of the latest developments of nano-scale surface characterization technique. In addition to being able to measure the nano-scale topological features of sample surface, it can also provide a materials mechanical contrast, although only semi-quantitative. In this dissertation, a truly quantitative measurement of the mechanical properties at nano-scale using tapping mode AFM is developed. The tip-sample interaction force during the nano-indentation process is calculated based on the numerical inversion of the governing integral equation of tapping mode AFM. The modulus of the sample is then calculated by fitting the interacting force to appropriate contact mechanics. The effect of experimental setting for the nano-scale modulus mapping based on the developed method is systematically studied and a high amplitude, low setpoint and a driving frequency slightly lower than cantilever resonance frequency setting is recommended.

Tapping mode AFM measures a polymer’s mechanical response in the millisecond range. Due to the viscoelastic nature of epoxy, the mechanical response of epoxy in
much greater time scales is very different. As a result, the mechanical properties of epoxy used in adhesive anchors for load bearing structures can’t be simply obtained through modulus measurement. We performed both long term and short term creep tests on two different commercially available resins and found it is possible to predicate the long term creep behavior from short term tests for both of the resins. One of the adhesive resins showed nonlinear creep behavior. Its creep speed was shown to be dependent both on the stress level and the apparent compliance in a straightforward relationship.
CHAPTER 1
INTRODUCTION

Overview

This dissertation focused on the characterization of the mechanical properties of epoxy resin at two opposite ends of time and size domains. As a viscoelastic polymer, the mechanical response of epoxy resin at very short times (~ms) or long times (years) will be very different. On the other hand, with the emerging application as the matrix material for nano composites, methods to measure the mechanical property variations at the nano-scale are quite different from methods used to measure those properties at a macroscopic scale. The first half of this dissertation focuses on the development of a robust method for nano-scale and micro-second interaction time modulus measurement on soft materials. Although this method was developed to reveal the modulus variation of an epoxy resin at the beginning, it has evolved into a very reliable tool for nano-scale force measurement. Modulus measurement is just one of its show case applications. The second half of this dissertation focused on the prediction of long term creep and potential failure of epoxy adhesive system used in adhesive anchor systems.

Nano-scale Modulus Measurement

The Requirements and Problems for Nano-scale Materials Characterization

Epoxy resins are one important class of polymer that enjoy many real life applications including coatings, adhesives and composite matricies. One reason for its popularity is due to its generally good mechanical properties.

As the technology advances, the thin interface between the epoxy resin matrix and reinforced particles or fibers has been showing more and more importance. This thin
layer can be less than a few hundred nanometers thick yet it shows varying properties on the nano-scale. ¹

In the meantime, inspired by the unique properties of nano-scale phase separated materials such as blocky polymers, epoxy resins with nano-scale mechanical and compositional differences have also been reported. ²

With all of the advances in nanotechnology associated with epoxy resins, there’s a clear need for a robust method to quantitatively measure the nano-scale properties of new types of materials. Atomic force microscope (AFM) is one of the most suitable instruments for nano-scale mechanical measurement due to its high resolution, ease of use and relatively simple sample preparation requirement ³. Quantitative measurements of sample surface properties have been the privilege of contact mode AFM, which is one of the two primary operation modes of AFM. The other operation mode is the dynamic mode, in which the probe tip only touches the sample surface a small fraction of the time during the measurement while the probe tip is dragged along the sample surface during the whole measurement. In addition, dynamic AFM utilizes a much stiffer probe cantilever than contact mode, so that it is less prone to snap onto the sample surface upon contact ⁴. However, due to the more complicated underlying physics of dynamic mode, robust and truly quantitative mechanical measurement are still a challenge, especially for amplitude modulation AFM, also called tapping mode AFM. This technique remains the most widely available operation mode of noncontact AFM.

Our Solution for nano-scale Modulus Characterization

To address these problems, we reviewed all the current efforts on quantitative tapping mode measurement and picked a flawed, but the most promising approach as the basic framework for our quantitative measurement method. With both theoretical
modification to the framework and careful attention to the experimental details, a robust measurement and data processing method based on tapping mode AFM was developed. The surface modulus and the adhesion energy between probe tip and sample surface can be accurately measured with a resolution only limited by probe tip size. The application of this method is not only limited to epoxy resin, but in fact can be applied to a wide range of polymers as well.

**Long Term Creep Prediction**

On the other hand, adhesive anchors, composite flywheels and wind turbines are examples of the well-established usage of epoxy resin as part of materials used in the sustained load structures. Such structures' stability and safety over their service life time is very critical, yet due to the viscoelastic nature of the epoxy resin, the mechanical properties of epoxy resin will change overtime\(^5\). In fact, the cause for the 2006 ceiling collapse accident that crashed on people inside a car in the interstate 90 connector tunnel in Boston is, according to the accident report, due to the creep of the epoxy resin over time\(^6\).

Since the service life time of load bearing structures generally are expected to be more than a few years it is not economical to test their performance over their entire service time. Accelerated testing, which can be performed in a relatively short time and can give a reasonable good service time prediction, are needed.

With the collaboration of people from the Department of Civil Engineering, an accelerated test method has been applied to two different commercially available resins. During the study an interesting creep speed dependence on the apparent compliance and stress level was found, based on which a prediction method for the long term creep behavior of the adhesive was recommended.
CHAPTER 2
BACKGROUND OF ATOMIC FORCE MICROSCOPE

Ever since more than two decades ago when the first AFM was invented at IBM\textsuperscript{7}, AFM has evolved into one of the most widely used nanotechnology tools for imaging, characterization and even manipulating materials at the nano-scale. Its flexibility on sample preparation allows the imaging of the nano-scale topological features of many different systems, ranging from semiconductor devices to bimolecules in water\textsuperscript{8,9}

It is also very versatile, capable of not only imaging topological features but also revealing the material’s contrast\textsuperscript{10}, direct manipulating matter at the molecular level\textsuperscript{11} and even measuring intermolecular forces\textsuperscript{12}.

**Operation Principles of AFM**

**Contact Mode AFM**

A single diagram showing the basic principles of contact mode AFM is shown in Figure 2-1. A cantilever with a very sharp tip size is brought very close to the sample surface so that the interaction force between the probe tip and the sample surface can deflect the cantilever arm. The small deflection is then amplified by a laser optically level and detected by an array of photodiodes. If the tip is dragged along the sample surface at a constant height, the topological as well as the material property variation of the sample at the point of contact will lead to a change of the cantilever deflection and thus image contrast is obtained. To prevent the tip or sample from damaging or colliding the tip onto sharp topological features, in practice a feedback loop is used to maintain a constant cantilever deflection by adjusting the cantilever height. The variation of height changes is then recorded to obtain the height image, showing topology information of the sample surface.
While well developed, contact mode AFM has a few limitations\textsuperscript{4}. During imaging, the tip is constantly pushing against the sample surface and dragged along and the resulting interaction force can damage delicate and fragile biomolecules, e.g. DNA, protein or cause viscous flow of the sample. In addition, to obtain high cantilever sensitivity in contact mode AFM, the effective spring constant of the cantilever must be comparable to the force gradient between tip-sample interactions so that small changes in interaction forces can lead to detectable cantilever deflection. If the cantilever used in contact mode AFM is too soft, the tip will snap into the sample when the attractive force gradient is larger than the cantilever spring constant, making it hard to obtain accurate attractive force measurements.

**Dynamic AFM**

Dynamic AFM was one of the approaches developed to address the aforementioned problems. In dynamic AFM, the cantilever is actively driven by an external force near its resonance frequency. By operating the AFM in a dynamic mode, the probe tip only touches the sample surface a small fraction of the time during the measurement, which results in a more gentle interaction between probe tip and sample surface. The average interaction force in dynamic AFM can be one to two orders of magnitude smaller than the average interaction force in contact mode AFM\textsuperscript{13}.

The external driving force can be a small piezo at the base of cantilever holder or external magnetic field if the cantilever is coated with a lever of a thin layer of ferromagnetic materials\textsuperscript{13}. The result is that the cantilever is oscillating up and down from its resting position (the position the tip will be if it is not oscillating) during operation. As the resting cantilever position is lowered by the instrument’s electronic system, the nearest tip-sample surface distance which is when the cantilever reaches
its downward maximum amplitude will also be reduced. When the tip-sample distance is in the range of a few nano-meters, interaction forces between the sample surface and the probe tip such as Van der Waals force or capillary forces will start to manifest and affect the cantilever motion. The cantilever vibration amplitude, frequency and phase shift are all sensitive to small changes from the tip sample interaction forces.

From here two type of operating modes can be obtained depending on which parameter is used in the feedback loop lock-in. If the amplitude is kept constant and the frequency shift and phase is monitored, the AFM is operating in the frequency modulation (FM) mode. On the other hand, if the frequency is kept constant and changes in amplitude and phase are recorded, the AFM is operating in the amplitude modulation (AM) mode, also called tapping mode. Both of these two operation modes are commercially available and can be applied to many different materials. The choice of operational mode is not arbitrary for a specific application and the quality factor of the cantilever plays an important role. When operating in water or air, due to the viscosity of water or air, the quality factor of the cantilever ranges from around 10 to a few hundreds while if the AFM is operated in ultra-high vacuum (UHV), the quality factor of the cantilever can be more than tens of thousands. The range of the quality factor determines both the feedback response speed and the detection sensitivity. The detection sensitivity is proportional to the inverse square root of the quality factor for both AM AFM and FM AFM. The feedback response speed is different for the two systems. For AM AFM, the feedback system is fast when the cantilever is operating in air or water with lower quality factor, while very slow if operated in UHV where the
cantilever quality factor is high. On the other hand, FM AFM will have a fast response only if the quality factor of the cantilever is very high.

As a result, although the variation of the frequency shift can be measured at much higher accuracy compared to changes in amplitude, the added complexity of UHV and the additional sample requirement make AM AFM a more popular choice for polymers, DNA and protein characterizations.

**Force Measurement**

**Contact Mode**

Apart from nano-scale imaging, AFM can also be used to measure forces between solids\(^{16}\). Assuming the effective spring constant of the cantilever is \(K\) and the cantilever deflection is \(Z\), then the overall force the cantilever experiences can be calculated as \(F=K\times Z\). If the relative position between the cantilever and the sample surface is not changed in the horizontal direction but in vertical direction, the deflection of the cantilever due to the tip sample interaction forces will thus depend on the tip sample distance. Please note that only the relative position between the tip and sample is needed to be changed, some instruments move the stage of the sample while others changes the height of the cantilever itself. In this dissertation, it is assumed the movement is due to the cantilever.

If the sample is infinitely hard, the deflection of the cantilever will be purely due the height of cantilever itself and thus the cantilever height changes will be equal to the cantilever deflection. The cantilever height vs. cantilever deflection plot will be linear once the tip touches the surface. Figure 2-2 shows the cantilever height vs. cantilever deflection plot when more complicated tip sample interactions forces are present. The tip sample interaction force is shown on the right. There’s no attractive force but a long
range attractive force exists before the tip reaches infinite hard sample surface. As the cantilever is pushed towards sample surface, the increasing repulsive forces deflect the cantilever gradually until the repulsive force reaches its maximum and any further decrease of the cantilever height lead to a linear deflect increase as in the case the infinitely hard surface\textsuperscript{17}.

As a result, the real tip sample distance is the total cantilever deflection minus what the cantilever deflection would be if the sample is infinitely hard, which is the linear line on the left, shown in Figure 2-2. Combined with the corresponding force cantilever experienced, the tip sample interaction can be calculated.

**Dynamic Mode**

The physics are fairly simple for contact mode force measurements. However, the jump-to-contact problem that occurs when the attractive force gradient is greater than the soft cantilever spring constant makes the measurement of the details of the attractive region difficult\textsuperscript{18}. Dynamic AFMs which utilize a much stiffer cantilever, can overcome the attractive force gradient while still maintaining a high measuring sensitivity\textsuperscript{13}. In addition, the possibility of maintaining a light interaction force during the measurement makes it possible to obtain measurements of a higher solution\textsuperscript{19}.

The challenge for dynamic AFM force measurements originates from the more complex physics governing the tip motion\textsuperscript{20}. The cantilever used in dynamic AFM generally has a rectangular shape with the tip having radius less than 10 nm located at the free end of the cantilever. Figure 2-3 shows the motion of the cantilever probe.

An external driving force provides the vibrating energy to the cantilever and the harmonic motion of the cantilever will be perturbed in the presence of tip sample interactions. To vigorously solve the equation of motion of such a system is very hard
and luckily it has been shown that the cantilever motion can be viewed as a point-mass model with an effective spring constant $K_c$ if the driving frequency is close to the fundamental resonance frequency of the cantilever beam\textsuperscript{21}. With such an approximation, the equation of motion of the cantilever probe can be written as

$$m \frac{dz^2}{dt^2} = -k_c z - \frac{m \omega_0}{Q} \frac{dz}{dt} + F_{ts} + F_{drive} \cos \omega t$$

(2-1)

Here $k_c$ and $m$ are the effective spring constant and effective mass of the cantilever, $\omega_0$ is the free resonance frequency of the cantilever, and $Q$ is the quality factor of the cantilever. $F_{ts}$ is the tip sample interaction and $F_{drive}$ is the external driving force. For AM AFM, the external driving force is fixed during operations $F_{drive} = F_0 \cos \omega t$ where $\omega$ is the driving frequency and $F_0$ is the initial force. The effective mass and the $F_0$ can be related to experimentally available values as: $m = \frac{k}{\omega_0^2}$ and $F_0 = \frac{A_0 \omega_0}{Q}$.

While in FM AFM, the motion of the tip is monitored, amplified, phase shifted and sent back as a self-driving system, which will keep the cantilever always vibrating at its resonance frequency at fixed amplitude.

The calculation method of tip sample interactions forces from FM AFM was already established base Sader’s theory frame work\textsuperscript{22} and results in very successful application\textsuperscript{23}. Detailed discussion of the principles of FM AFM is beyond the scope this dissertation. The following discussion will be limited to AM AFM unless there’s something in common between the FM AFM and AM AFM.

In AM AFM, the amplitude and phase changes have been related to the average tip sample interactions forces during each oscillation cycle. It has been shown that

$$\frac{k_{eff}}{m} = \omega^2 + \cos(\varphi) \frac{F_0/m}{A}$$

(2-1)
here $k_{eff}$ is the average tip sample interaction weighted by tip sample distance over one oscillation cycle\textsuperscript{24}. Apparently values calculated this way lack a clear definition.

In addition, the energy loses $E_{dis}$ during each oscillation cycle can also be calculated from phase and amplitude values using the equation\textsuperscript{25}:

$$\sin \theta = \frac{\omega A(\omega)}{\omega_0 A_0} + \frac{QE_{dis}}{\pi k A_0 A(\omega)} \quad (2-3)$$

Using a similar energy approach it is possible to tell the nature of the energy dissipation process by the shape of the energy dissipation as a function of amplitude\textsuperscript{26}. The limitation of these approaches is that all these values, from average interaction forces to energy dissipation depends on the actual operation settings of the AM AFM and thus the physical properties of the sample being tested can’t be decoupled and calculated.

Another approach is to try to use the similar approach as in the contact mode force measurement. The cantilever height is ramped from far from sample surface until very close to the sample surface where the amplitude of the cantilever vibration is greatly reduced; in the meantime, the phase and amplitude values are recorded as a function of height. The obtained amplitude-phase-distance (APD) curve will then be used for a tip-sample interaction force reconstruction. Due to the nonlinear nature of the tip sample interaction and the complexity of the equation of motion of the probe, such conversion is not straightforward. Considering the tip sample interaction force is much smaller than the restoring force from the cantilever itself, it has been shown that the tip motion of dynamic AFM can be considered as a weakly perturbed harmonic oscillator\textsuperscript{27}. Based on this assumption, the cantilever motion can be approximated as

$$x(t) = A \cos(\omega t + \varphi) \quad (2-4)$$
Plugging equation 2-4 into equation 2-1 and using Fourier analysis two integral equations can be obtained.

\[
y(Z) = \int_0^{2\pi} F_{even}[Z + A \cos \theta] \cos \theta d\theta \quad (2-5)
\]

\[
y2(Z) = \int_0^{2\pi} F_{odd}[Z + A \cos \theta] \sin \theta d\theta \quad (2-6)
\]

The first equation is related to the conservative forces while the second is related to nonconservative forces. \(y(Z)\) and \(y2(Z)\) are values calculated from amplitude, phase, quality factor and driving frequency. These set of integral equations are valid for both AM AFM and FM AFM and all the published efforts to our knowledge to reconstruct the tip sample interactions are based on inverting these two integral equations. As mentioned earlier, the inverse of these two equations for FM AFM is solved quite nicely but for AM AFM, there are still limitations to current approaches.

Under the assumption of a large amplitude compared to the tip-sample interaction range, Holscher reduced the first integral equation into an integral equation that has an analytical inverse solution\(^{27}\). But the assumption limited Holscher’s approach on attractive forces. Katan et al. and Lee et al. both first applied Laplace transforms on the integral equations and were faced with the problem of evaluating the inverse Laplace transform of a modified Bessel function, which is the method used for FM AFM inversion\(^{20,28}\). Due to the difference between AM AFM and FM AFM, the subsequence steps are different. Katan showed that by ignoring the fact that the amplitude in AM AFM change during the ADP curve, it is possible to reconstruct tip-sample interaction forces using the same kind of approximation used in FM AFM. They acknowledged the potential error associated with the difference. Lee et al. expanded the modified Bessel function into a Taylor series and obtained two linear differential equations of infinite order\(^{20}\). However, due to the exponential growth of the modified Bessel function, the
number of orders needed for a high accuracy inversion can be quite high when the
driving amplitude is large. In fact, the author only showed examples at very small free
amplitude values.

Hu et al. used Chebyshev polynomials to approximate the tip-sample interaction
and showed some promising result\textsuperscript{29}. Their theory framework placed no restriction on
the amplitude of the cantilever and was shown to be able to handle jumps. The
limitation of their method is a lack of high convergence even if as many as 40 terms are
used.

**Dual Stability of the Oscillation State in AM AFM**

The stable solution for equation 2-1 for a given tip sample interactions and
cantilever height in AM AFM is not always unique. Sometimes more than one solution
will coexist\textsuperscript{30,31}. Each solution that the tip motion follows is called a possible operation
state and the tip tends to stay in the same state during the measurement until the
perturbation from noise is strong enough to push the probe into another state. The
needed perturbation to change the operation state depends on the drive amplitude,
frequency and the cantilever height. During the ramping for ADP curve measurement,
merely instrument feedback perturbation can sometimes lead to the jump from one state
to another. A typical example ADP curve of the jump is shown in Figure 2-4, which is
obtained on a polystyrene (PS) thin film. Note the curves look noisier around the jump.

A direct consequence of the existence of two stable states is that at a given
cantilever height there are two possible amplitudes which corresponding to two different
tip sample nearest distances\textsuperscript{32}. For imaging, a sudden jump from a low amplitude state
to high amplitude state can lead to a sudden increase of tip indentation to the sample
surface, which can potentially damage the sample. For force measurement, such jump
make it very hard to obtain accurate the derivative of phase and amplitude against nearest tip sample distance, which are the fundamentals of several force measurement theory frameworks mentioned before.

**Contact Mechanics**

The interpretation of the reconstructed tip sample interactions forces need a proper understanding of the underlying interactions. In the indentation part of the interactions forces, the effective surface modulus of the sample can be related to the sample deformation. A proper analysis using contact mechanics model is needed to make the conversion possible.

The contact mechanics are widely used for AFM force measurement analysis. A few assumptions are implied when using the several most popular contact mechanics models. First, the contact is between two elastic bodies. Second, there’s no friction between the two bodies. The Derjaguin approximation is also usually assumed, which states that the if indentation or the interaction range between the two body is very small compared to the curvature of the bodies, the curved the surfaces can be considered as two parallel planes. In addition, for the AFM application, if the sample is a soft material such as a polymer or biomolecule, the stiffness of the tip is much greater so that the deformation of the tip during the contact can be ignored.

Depending on the relative magnitude of the adhesion force and repulsive force during tip sample contact as well as the nature of the contact mechanics, the most suitable contact mechanic model varies for a given interactions. When the load P is far larger than the adhesive force between the two contact bodies, the adhesive force can be ignored and the simplest Hertz model is most suitable. Such a scenario is more
common during the nanoindentation test but for AFM force measurements the adhesion force is generally too large for the Hertz model.

When adhesion force is needed to be taken into account for AFM force measurements, the Johnson-Kendall-Roberts (JKR) model and the Derjaguin-Muller-Toporov (DMT) model are the two most widely used models providing analytical solutions between the deformation and applied load\textsuperscript{35,36}. The DMT model, which is most applicable for stiff interactions are low adhesion, added long range attractive force into consideration but assume that the added adhesion won’t affect the contact deformation. On the other hand, in the JKR model the adhesion is thought to present only within the contact area and will also affect the contact deformation. The JKR model works best when the contact bodies are soft and adhesive.

The contact mechanics are more complicated in real situations. The adhesion force will be long range as in the DMT model and it will also affect how the contact surface deforms as in the JKR model. To approximate the real situation, Maugis considered the adhesive force has the form of Dugdale potential and introduced an elasticity parameter $\lambda$ which compares the surface force’s range to the elastic deformation they cause\textsuperscript{37}. It turns out the DMT and JKR models are the extreme cases of the Maguis-Dugdale (MD) model. When $\lambda$ is less than 0.1, DMT is very suitable while JKR can be used when $\lambda$ is more than 5. The regions in between where $\lambda$ ranges from 0.1 to 5 is called the Maugis-Dugdale (MD) region. The distribution of different contact mechanisms according to the elasticity parameter and the load to adhesion ratio is shown in the adhesion map in Figure 2-5\textsuperscript{38}. 
Although the MD theory is very general it is very hard to be directly applied to experimentally obtained forces in measurement data. Carpick et al. solved this problem by providing an excellent approximation to the solution of MD theory\textsuperscript{39}. The experimentally obtained load vs. contact area can be fitted against Carpick’s model to obtain $\lambda$. Once $\lambda$ is determined, all the other interesting parameters can then be calculated. Pietrement et al expand Carpick’s method so that load vs. indentation data can be used obtain $\lambda$ as well\textsuperscript{40}.

**AM AFM Force Measurement for Modulus Mapping and More**

In spite of all the developments of AFM, an accurate force measurement based on the most popular AFM for soft materials, the AM AFM is still lacking. In the following chapter we will present the theory of our force measurements based on AM AFM. In chapter 4 we will discuss the experimental details for our most robust force measurements based on our method and also show the applications of modulus mapping on a polymer blend. The current limitation of the method will also be discussed.
Figure 2-1. Schematic of a contact mode AFM (after H-J, Butt, et. al. 2005)

Figure 2-2. A typical cantilever height (Zp) vs. cantilever deflection (Zc) plot shown on the left and corresponding tip sample distance (D) vs. cantilever deflection(Zc) plot shown on the right. (after H-J, Butt, et. al. 2005)
Figure 2-3. Schematic that showing the dynamic AFM tip motion (after Hu et al.)

Figure 2-4. Jump in the ADP curve. Obtained on a PS thin film

Figure 2-5. The Adhesion map (After Johnson KL et al. 1997)
Figure 2-6. Load vs indentation plot for different contact mechanics models (After Pietrement et al, 2000)
CHAPTER 3
THE THEORY OF THE FORCE MEASUREMENT METHOD USING AM AFM

Overview

Amplitude modulation AFM is one of the most versatile tools for surface imaging and composition contrast with a nanoscale resolution. However, due to the nonlinear interaction between the tip-sample interactions, the composition contrast is semi-quantitative and the topological information is also affected\(^4,10\). To overcome such a constraint, new types of measurement methods were developed which showed very promising results\(^41\). However, such new methods generally need hardware upgrades to current AFM instruments, which limits the availability of this method.

The other approach to the problem is to reconstruct the tip-sample interaction forces using tapping mode\(^{20,27-29}\). In this approach, the vibration frequency of the probe is kept constant and the cantilever sample distance is ramped from far above the sample surface to very close to the sample surface. The variations of amplitude and phase value are recorded in the process. The obtained amplitude-phase-distance (APD) curve will then be used for tip-sample interaction force reconstruction. Due to the nonlinear nature of the tip-sample interaction, only until recently two types of theory frameworks for the reconstruction were published. One used Laplace transform and modified Bessel functions, similar to the method used in quantitative FM force spectroscopy\(^{20,28}\). However, as pointed out by one of the paper’s authors, the assumption of constant oscillation amplitude is used in the derivation of the formulae and the actually reduction of amplitude during the ramp can be more than 50%. The other method is to use Chebyshev polynomials to approximate the tip-sample interaction\(^{29}\). Although in their paper as much as 40 terms were needed for reasonable
convergence, there are fewer assumptions and can even handle jumps in the APD curve to a certain extent. However, to extract any useful physical values of the sample itself, the reconstructed tip sample interaction forces have to be of much higher accuracy.

In this section of the work, by dividing the tip-sample interactions during tapping mode AFM into two or more regions, with each region approximated by a Chebyshev polynomials, we were able to reconstruct the AFM tip sample interactions, which is highly converged and accurate enough from which the sample surface modulus can be measured within 15% precision.

**Theory**

**Existing Background**

In tapping mode AFM, the cantilever motion can be described by equation 1

\[
\left(\frac{\omega}{\omega_0}\right)^2 \frac{d^2 x}{dt^2} + \frac{\omega}{Q\omega_0} \frac{dx}{dt} + x = \frac{F_{ts}}{k_c} + \frac{F_{drive}}{k_c}
\]  

(3-1)

where \(k_c\) is the effective spring constant of the cantilever, \(\omega_0\) is the free resonance frequency of the cantilever and \(Q\) is the quality factor of the cantilever. The external driving force \(F_{drive} = F_0 \cos \omega t\) where \(\omega\) is the driving frequency and \(F_0\) is kept constant. \(F_{ts}\) is the tip sample interaction.

One of the basic principles of tapping mode AFM is to assume the cantilever motion can be approximated by a harmonic motion\(^4\). Based on this assumption, the cantilever motion can be approximated as

\[
x(t) = A \cos(\omega t + \phi)
\]  

(3-2)
where $A$ and $\varphi$ are the amplitude and phase lag of the cantilever motion and are the observed values in from tapping mode AFM experiments. Such assumption is generally satisfied under typical operation conditions in the air.

$F_{ts}$ is generally a nonlinear function of tip sample distance. It depends on both cantilever tip position and tip speed and can be separated into $F_{ts}(x, \dot{x}) = F_c(x) + F_{nc}(x, \dot{x})$. In addition, during one period of harmonic motion of the cantilever, $F_{ts,\text{approach}}$ can be different from $F_{ts,\text{retract}}$. $F_{ts}$ can also be decomposed as

$$F_{ts} = F_{\text{even}} + F_{\text{odd}}$$

where $F_{\text{even}} = (F_{ts,\text{approach}} + F_{ts,\text{retract}})/2$ and $F_{\text{odd}} = (F_{ts,\text{approach}} - F_{ts,\text{retract}})/2$. Plugging Equations 3-1 and 3-2 into Equation 3-3 and using Fourier analysis, for a given cantilever sample distance $Z$, we will have:

$$-\pi k_c A \left( \frac{\Omega}{\Omega_0} - 1 + \frac{\cos \varphi}{A/A_0} \sqrt{\frac{\Omega^2}{Q^2} + (1 - \Omega^2)^2} \right) = \int_0^{2\pi} F_{\text{even}} [Z + A \cos \theta] \cos \theta d\theta$$

$$-\pi k_c \left( \frac{\Omega A}{Q} - A_0 \sin \varphi \sqrt{\frac{\Omega^2}{Q^2} + (1 - \Omega^2)^2} \right) = \int_0^{2\pi} F_{\text{odd}} [Z + A \cos \theta] \sin \theta d\theta$$

where $\Omega = \frac{\omega}{\omega_0}$, $A_0$ the free amplitude of the cantilever motion and $Z + A \cos \theta$ is the instantaneous tip sample distance, denoted $z$ below.

Here, the left side of equations 3-4 and 3-5 contain only experimentally accessible values from tapping mode AFM. To invert equation 3-4 and 3-5 using data from APD curves, $F_{\text{even}}$ and $F_{\text{odd}}$ must be a unique function of $z$, independent of the cantilever
sample distance. If $F_{nc}(x, \dot{x})$ is an odd function of the tip velocity, valid for interactions such as surface hysteresis and viscoelasticity of polymer, $F_{\text{even}}(z)$ can be reconstructed by inverting equation 3-4\textsuperscript{42}. However, $F_{\text{odd}}$ typically depends on the cantilever sample distance. We will reconstruct the $F_{\text{even}}(z)$ first and discuss the issues on the reconstruction of $F_{\text{odd}}$.

Hu used Chebyshev polynomials to approximate $F_{\text{even}}$ as:\textsuperscript{29}

$$F_{\text{even}}(z) = \sum_{n=0}^{N} C_n T_n(z)$$

(3-6)

where $T_n(z)$ is the Chebyshev polynomials of the first kind linearly mapped to effective tip sample interactions range, which are from the lowest tip sample distance $Z - A$ (denoted as $D_0$) to a few nanometers above the sample surface (denoted as $D_2$ in the following sections) where the tip sample interaction is negligible. Inserting equation 3-4 into equation 3-2 and switching the order of integral and summation gives us

$$\gamma(D_0) = \sum_{n=0}^{N} C_n \int_{0}^{2\pi} T_n(Z + A \cos \theta) \cos \theta \, d\theta$$

(3-7)

where $\gamma$ is the result of the left side of equation 3-4. For each data set of APD curve, there is once such equation. Combining all these equations gives us a set of linear equations, from which the $C_n$ can be solved in a min-max manner.

Hu’s method showed promising results. However, since Chebyshev polynomials in essence are still Fourier series, it works best for smooth functions\textsuperscript{43}. If there are discontinuities in the functions’ derivatives or even in the function itself, the number of terms needed for a good approximation will increase greatly and the reconstructed force will show Gibbs effect\textsuperscript{44}. Unfortunately in tapping mode AFM, during one oscillation of the cantilever motion, the tip usually experiences a few regions of different interactions.
For example, if the interactions follow Derjaguin-Muller-Toporov (DMT) model, the transition of van der Waal force to elastic repulsive force is pretty sharp. If the tip sample interaction follows the Johnson-Kendall-Roberts (JKR) model, there will even be a jump in the interactions force profile.

As a result, if $F_{even}(z)$ is expanded into a single Chebyshev polynomials series, as much as 40 terms are needed even in numerical simulations to achieve an acceptable converge. In addition, if only a few terms are available, high frequency variations due to noise will be smoothed out automatically. When too many terms of Chebyshev polynomials are used to compensate for the sharp transitions, it can adjust all the available coefficients trying to “remember” the sharp transitions as well as the noise. In fact, the reconstructed forces from experimental values reported by Hu showed a lot of waves using 40 terms, which is a sign that the coefficients of the high frequency component of the Chebyshev polynomials expansion were disrupted by experimental noise.

**Multi-region Chebyshev Expansion**

To solve this problem, we divided $F_{even}(z)$ into separated smooth regions where each region was approximated by a single Chebyshev expansion. Let us first consider the situation that there is only one sharp transition in $F_{even}(z)$ located at $z = a$ and only two separate Chebyshev expansions are needed. If the first expansion has $N$ term and the second has $M$ term, we have:

$$F_{even}(z) = \sum_{n=0}^{N} C_n T_n(z) \mid_{z>a} + \sum_{m=0}^{M} C'_m T'_m(z) \mid_{z\leq a}$$  \hspace{1cm} (3-8)
For the APD data that $D_0 > a$, which means the tip stays in the first part of the tip sample interaction during the whole oscillation circle, then equation 3-7 is still valid and is rewritten here as:

$$
\frac{\gamma}{2} = \sum_{n=0}^{N} C_n \int_{0}^{\pi} T_n(Z + A \cos \theta) \cos \theta \, d\theta
$$

(3-9)

Note that the even property of $F_{even}(z)$ is used here to transform the integral upper range from $2\pi$ to $\pi$. The mapping range of $T_n$ is still from $D_0$ to $D_2$. Using those APD data, $C_n$ can be solved.

For APD data that $D_0 \leq a$, the tip experienced the second part of the interactions during one oscillation circle so that the integral equation becomes

$$
\frac{\gamma}{2} = 
\sum_{n=0}^{N} C_n \int_{0}^{(Z+A \cos \theta)=a} T_n(Z + A \cos \theta) \cos \theta \, d\theta + 
\sum_{m=0}^{M} C'_m \int_{(Z+A \cos \theta)=a}^{\pi} T'_m(Z + A \cos \theta) \cos \theta \, d\theta
$$

(3-10)

Here the mapping range of $T_n(z)$ is from $a$ to $D_2$ while the mapping range of $T'_n(z)$ is from $D_0$ to $a$.

Setting $I_n = \int_{0}^{(Z+A \cos \theta)=a} T_n(Z + A \cos \theta) \cos \theta \, d\theta$ and $I'_m = \int_{(Z+A \cos \theta)=a}^{\pi} T'_m(Z + A \cos \theta) \cos \theta \, d\theta$ and plugging in the $C_n$ that’s already solved, we have

$$
\frac{\gamma}{2} - \sum_{n=0}^{N} C_n I_n = \sum_{m=0}^{M} C'_m \int_{(Z+A \cos \theta)=a}^{\pi} T'_m(Z + A \cos \theta) \cos \theta \, d\theta
$$

(3-11)
Combining all the APD data where $D_0 \leq a$, we have a second set of linear equations, from which $C'_n$ can be solved. With $C_n$ and $C'_m$ solved, so are the tip sample interactions.

Now we expand the method to the cases that multiple regions in $F_{even}(z)$ are separated by sharp or discontinuous transitions at $a_1, a_2, a_3 \ldots$ where $a_1 > a_2 > a_3 \ldots$. Based on the same principles discussed earlier in this section, each region can be approximated by a Chebyshev expansion and their coefficient can be solved in a recursive manner.

To solve

$$y/2 = \int_0^\pi F_{even}[Z + A \cos \theta] \cos \theta d\theta \quad (3-12)$$

Let:

$$F_{even}(z) = \sum_{n=0}^{N_1} C_n T_n(z)|_{z>a_1} + F_{sub}(z)|_{z\leq a_1} \quad (3-13)$$

For all APD data with $D_0 > a_1$, there's a $y/2 = \sum_{n=0}^{N} C_n I_n$ as shown in equation 15. By combining all of these equations, $C_n$ can be solved and thus the first smooth region is approximated. Now set $y' = y/2 - \sum_{n=0}^{N} C_n I_n$ for the rest of APD data, where the integration range of $I_n$ is $[0, (Z + A \cos \theta) = a]$ instead of $[0, \pi]$.

So now we just need to solve

$$y' = \int_{(Z+A \cos \theta)=a}^{\pi} F_{sub}[Z + A \cos \theta] \cos \theta d\theta \quad (3-14)$$

By repeating the same process to $F_{sub}(z)$ as to $F_{even}(z)$, changing $a_1$ to $a_2$, $N_1$ to $N_2$, the Chebyshev expansion coefficient of the second smooth region can be solved.
Repeating this process until the $F_{sub}$ becomes the last smooth region and solving it as a single Cheby expansion, the whole range of $F_{even}$ can be solved.

**Determine the Positions That Separate the Interactions into Different Regions**

Although there’s no restriction mathematically on the position of $a_i$ to perform the previous calculation, only an accurate estimation of the location of the transition in the tip sample interactions can help us separate the interactions into smooth regions.

Equation 3-6 shows that $y$ in fact is the tip sample interactions averaged with a weight of $\cos \theta$ during one oscillation. When the interactions range first exceed the position of $a$, the continuity of $y$ at $D_0 = a$ will depend on the continuity of $F_{even}(z)$ at $z = a$. An accurate description of the relationship between the continuity of $F_{even}$ and $y$ is hard to obtain at the moment. Examination of the weight $\cos \theta$ showed that more weight is on the interaction forces near the nearest tip-sample distance $D_0$ where $\theta$ is near $\pi$. Thus if $F_{even}(z)$ has a local minimum at $z = a$, which usually indicating the change of interaction from attractive to repulsive, there will be a corresponding minimum at $D_0 = a$ in the derivative of $y$.

On the other hand, the Chebyshev coefficient $C_n$ of the interactions are indirectly calculated from solving the overdetermined linear equations, which in fact is to find the least square solution of the linear combination of the weighted integral of the Chebyshev expansions for $y$. If $y(D_0)$ is not smooth enough, it is not possible to reach convergence with a limited number of terms. From an experimental point of view, separating the $y(D_0)$ at the local minimum of the derivative of $y(D_0)$ will provide the
most smooth regions. As a result, we use the location where the local minimum of the derivative of $y(D_0)$ to as the $a$ in our calculation.

**Numeric Results**

Here we demonstrated the reconstruction of two types of interaction force profiles by our method. The first interaction force follows the DMT contact model and the second is a modified JKR contact models. We first used the assumed interaction force profile and governing integral equation 3-4 to directly calculate the dependence of $y$ value on cantilever height and then used our method to reconstruct the assumed interaction force profile through the $y$ value.

**DMT Model**

The DMT model is a conservative type of force, with one sharp transition, defined as a function of tip sample surface distance $z$:

$$F_{DMT}(z) = \begin{cases} 
\frac{-HR}{6z^2}, & z > a_0 \\
-\frac{HR}{6a_0^2} + \frac{4}{3}E^*\sqrt{R}(a_0 - z)^{1.5} & z \leq a_0
\end{cases} \quad (3-15)$$

Here $a_0$ is the intermolecular distance, $H$ is the Hamaker constant, $R$ is the radius of the tip and $E^*$ is the reduced modulus of the sample surface. The values taken in the calculation: $H=1e-19J$; $R=10e-9m$; $a_0=0.236e-9m$; $E^*=1e9GPa$.

After defining the specific force profile, we numerically solved equation 3-1 to obtain $A$, $P$ and $Z$. Instead of plugging in $A,P,Z$ values from the simulation result into the left side of equation 3-4 to get the $y$ value, we used the right side part of equation 3-4 and the $A$ and $Z$ obtained from the simulation to perform the integral to directly calculate $y$ for the reconstruction. The $y$ value calculated this way won’t be affected by any error...
introduced from numeric calculations, which is a better starting point to isolate the effect of how the integral inversion method works.

Figure 3-1 shows the $y$ value as a function of $D_0$ under the DMT model and Figure 3-2 shows the derivative of $y$ to $D_0$. Although the location of $a_0$, where the probe first touch the repulsive region of the interaction, is not very clear in $y(D_0)$, it is very clearly located in its derivative showing itself as the pointing local minimum, which was used for interactions force reconstruction. Figure 3-3 shows the reconstructed $F_{even}(z)$ with different terms in the two separated interactions regions, overlayed with DMT model.

Note that since $F_{DMT}(z)$ is a conservative force, $F_{even}(z) = F_{DMT}(z)$. The dashed line is the reconstructed force profile with 5 terms ($N=5$ in equation 3-6) of Chebyshev expansions for the first region of the interaction, which correspond to Van der Waals attractive force. Only 3 ($M=3$ in equation 3-6) terms are used for the repulsive region. We reached very good convergence of the repulsive region with only 3 terms. With 5 terms for the attractive force region, the place near $a_0$ has a poorer convergence due to that fact it is very close to the singularity of the assumed Van der Waals force form in the DMT model. When 10 terms are used for the first region and 5 terms used for repulsive region, excellent reconstructed interactions were achieved shown as a dash-dot line in Figure 3-3, which can barely be distinguished from the DMT model. The inserted plots are locally zoomed near the transition region.

**Modified JKR Model**

It can be summarized that the tip sample interaction during AFM on soft materials falls into the MD region most of the time. For a contact model that is more like the real
tip sample interaction during measurement on polymer samples, we used a modified JRK model. In this model, when the tip and sample are not in contact, the attraction between them follows the van der Waal attraction force. While when they are in contact, their interaction is considered to follow the JKR model. In addition, an hysteresis was added on purpose: during approach the sample surface won’t be deformed due to van der Waal attraction force while during retraction the sample surface will be deformed as in the case of the JKR model. The added hysteresis served as a gap between the DMT and JKR models. This model is still an over simplification of a more complicated model used by Greenwood and is a better representation of the real tip sample interaction than simple JKR and DMT model. The simplification for the simplicity of calculation and our simplified version still contains the main feature of Greenwood’s model.

The JKR model is defined as:

\[
F_{JKR}(z) = \begin{cases} 
0 & z \geq d_0 \\
\frac{4E^*a^3}{3R} - \sqrt{8\pi W_{JKR}E^*a^3} & z < d_0 
\end{cases} \quad (3-16)
\]

where \(E^*\) is the reduced modulus, \(R\) the tip radius, \(W_{JKR} = 2F_{ad}/3\pi R\) is the work of adhesion and \(F_{ad}\) is the adhesion force. \(a\) is the contact radius and \(z = -\frac{a^2}{R} + \sqrt{\frac{2\pi a W_{JKR}}{E^*}}\). \(d_0\) is defined differently for approach and retract. During approach, \(d_0 = 0\).

During retract, \(d_0 = \sqrt{\frac{2\pi a_{crit} W_{JKR}}{E^*}} - a_{crit}^2/R\) and \(a_{crit} = \left(\frac{\pi R^2 W_{JKR}}{8E^*}\right)^{1/3}\). The JKR model assumes there is no attractive force when the tip and sample surface are not in contact. Here we modify this assumption to add Van der Waals attractive force \(-\frac{HR}{6z^2}\) when the tip and sample surface is not in contact. The final approach and retraction
force is shown in Figure 3-4 where $F_{ad} = 4$ nN and the rest of the values are the same as in the DMT model. The hysteretic nature of $d_0$ making the approaching and retracting interactions different from each other and the $F_{even}(z)$ is the average of approach and retract also shown in Figure 3-4. Note the discontinuity and the sharp transition present in $F_{even}(z)$.

Figure 3-5 shows the $y$ value and Figure 3-6 shows its derivative under this modified JKR model. The location where the sharp transition and the discontinuity were clearly present in the derivative of $y$. Since there are two transitions we need to separate the $F_{even}(z)$ into three regions.

The dotted line in Figure 3-7 is the reconstructed $F_{even}(z)$ with 5+5+5 terms and it is in excellent agreement with the solid line in Figure 3-7 which shows the $F_{even}(z)$ of the modified JKR model force profile. For comparison, the dashed line shows the reconstructed force used a single 40 term Chebyshev expansion, in which almost all the rich information during the two transitions is lost.

In summary, our approach to inverse the integral equation to reconstruct the interaction forces can reach almost perfect convergence with very limited terms in each region. We will use this method in the next section on polymer surfaces.

**Experiments on Polymer Surfaces**

To demonstrate the algorithm in practical applications, we used it to reconstruct the $F_{even}(z)$ part of the tip sample interaction on a polystyrene(PS) surface and Poly(methyl methacrylate) (PMMA) surface. The PS and PMMA surfaces were spin coated on a small piece of silica wafer at 3000 rpm for 30 seconds from toluene solution at a concentration of 0.5 wt %. The surfaces were then annealed at 120 °C for 12 hours.
The roughness of the prepared surfaces had a RMS roughness around 0.2 nm measured from the tapping mode height image. Tapping mode AFM was performed at room temperature in air using a DIMENSION 3100 with a NanoScope V (Digital Instruments). A TESP cantilever from Bruker and a tip radius of 10 nm was used for reconstruction. The spring constant of the cantilever was determined as 38 N/m using Sader’s method. The free resonance $f_0$ of the cantilever measured 100 nm above the sample surface was 290.988 kHz and the quality factor was calculated by fitting the frequency sweep curves from 0.995 $f_0$ to 1.005 $f_0$. The free amplitude of the cantilever was set to 40 nm and the drive frequency was kept at the free resonance frequency of the cantilever. The background noise of the acquired APD curves was denoised by hard threshold wavelet denoise with a CDF 5/3 wavelet before reconstruction. $D_2$ was set to 5 nm above the position where the amplitude first started to vary away from free amplitude.

Figure 3-8 shows an example of the APD curve, Figure 3-9 shows the $y$ value calculated from the APD curve, and Figure 3-10 shows the derivative of $y$. This example was taken on the PS surface. The $a$ value was taken at the local minimum of the derivative of $y$.

Please note that the x axes in Figures 3-9 and 3-10 were shifted after the reconstructed force was obtained so that the greatest attractive force was located at the origin. The position of $a$ obtained this way agreed very well with the origin where the transition of interactions occur. With $a$ determined, each region of the interactions separated by $a$ was reconstructed by 10 Chebyshev series terms.
After the tip sample interactions were reconstructed from the APD curve, the repulsive region was fit using a generalized equation closely approximating the analytical solution of Maugis-Dugdale’s theory\textsuperscript{39,40}. This model can fit both interactions following a DMT or JKR model and those in between. The fitted model can provide the modulus of the sample surface as well as a $\delta$ value between zero and one indicating if the interaction is more DMT like or JKR like. Zero means pure DMT while one means pure JKR. Figure 3-11 shows reconstructed conservative tip sample interactions forces and the corresponding hybrid model fit. The calculated modulus of PMMA is 3.78 GPa while PS is 2.68 GPa, both of which are in the normal range of their bulk modulus and agrees well with values reported in the literature. In addition, the $\delta$ of both sample is around 0.9, indicating a high percentage of JKR type of interaction.

To test the accuracy of the reconstructed interactions, 25 APD curves were taken on a 5 by 5 grid of each sample. The grid separation is 10 nm. The grid shown on AFM height image is shown in Figure 3-12 and the corresponding reconstructed interactions for the PMMA surface were shown in Figure 3-13. The curves fall on each on very well.

The average modulus from 25 ADP curves from PMMA surface is $3.8 \pm 0.5$ GPa while the it is $2.6 \pm 0.4$ GPa on PS surface. The error range for both samples is within 15% of the measure value. Please note that we found the phase image for both the PS and PMMA surfaces showed microstructure domains with sizes around 20 nm and a phase difference of 2 to 5 degrees, indicating a certain degree of surface inhomogeneity that might contribute to the distribution of the measure modulus. In other words, if the surface is truly homogeneous, the accuracy of the measurement will be even higher.
The surface modulus of PS and PMMA film reported by other groups were 2.3 GPa and 3.7 GPa respectively, both of which agreed with our result.\textsuperscript{41}

**Discussion**

Although in theory we can separate the interaction forces in as many regions as one would want, there are not too many sharp transitions in most practical situations and the current experimental resolution limits our ability to reveal all the details. In fact we found two regions work pretty well in most of the time.

For the reconstructed force on the PS surface, although there is no apparent jump in the attractive region, careful examination showed that the slope first decreased, then increased. Such behavior showed close resemblance of the $F_{\text{even}}(z)$ in the modified JKR model used in this paper. Taking into account a $\delta$ very close to 1, the reconstructed interaction clearly indicates the nature of this tip sample interaction resembles the modified JKR model and shows our method’s ability to detect subtle variations in the tip sample interactions.

It is tempting to expand the current method to inverse the equation 3-5 so that the odd part of the interactions can also be reconstructed to give the whole picture of the tip sample interaction. However, $F_{\text{odd}}$ is generally not a unique function of $z$. One type of stronger assumption used in the literature has the form $F_{\text{odd}} = F_{\text{nc}}(z, \dot{z}) = -\dot{z}\Gamma(z)$, which can describe many physically interesting interactions. Please note that such an assumption is not valid in a JKR type of interaction, where part of the contribution $F_{\text{odd}}$ comes from hysteresis that is independent of $\dot{z}$. If such a form of $F_{\text{nc}}$ is incorporated into equation 3-5, the resulting integral equations is:
\[ y' = \int_0^\pi \Gamma[Z + A \cos \theta] \sin^2 \theta \, d\theta \] \hspace{1cm} (3-17)

where \( y' \) can be calculated from the APD curve. However, the major part of the tip sample interaction is when the tip is close to or even indents the surface, where \( \theta \) is near 0. As a result, \( \sin^2 \theta \), which acts as a weight inside the integral, is very small, greatly reducing the contribution of valuable tip sample interactions information to \( y' \).

Recall that the weight in equation 3-7 for \( F' \) is \( \cos \theta \), which actually increases in weight when the tip is interacting with the sample surface. This means the inversion of the integral equation 3-17 has much less of a tolerance on noise or error from the calculation of \( y' \) than that of the \( F'_{\text{even}} \) counterpart. If \( y' \) is as accurate as in the numeric calculation, we can easily use the same method to inverse the integral equation.

Unfortunately, due to the presence of experimental errors, any attempt to reconstruct the \( \Gamma(z) \) from \( y' \) calculated from experiment values did not provide any satisfactory result.

**Summary**

A method was proposed to measure the modulus of a polymer surface at nanoscale resolution with tapping mode AFM. This was accomplished by reconstructing the conservative tip sample interaction forces from an APD curve and fitting the interaction force profile to a hybrid model to calculate the modulus at the point where the APD curve is taken. The reconstruction method uses Chebyshev expansions to perform an inverse operation on the underlying integral equation and separate the interactions into smooth regions to solve the problem that Chebyshev expansions do not perform very well when there are sharp transitions. Numeric calculations showed
that the method is valid and experimental data demonstrates that we can achieve a modulus measurement of PMMA and PS surface within 15% accuracy.

Figure 3-1. The y value for the DMT model
Figure 3-2. The derivative of the y value for the DMT model

Figure 3-3. The DMT model and the reconstructed $F_{even}(z)$
Figure 3-4. The approach and retract force of the modified JKR model and their average $F_{even}(z)$

Figure 3-5. The $y$ value of the modified JKR model
Figure 3-6. The derivative of the y value of the modified JKR model

Figure 3-7. The $F_{even}(z)$ of the modified JKR model and the reconstructed forces
Figure 3-8. An example of the APD curve on a PS surface

Figure 3-9. The y value for the PS surface calculated from the APD in Figure 3-8
Figure 3-10. The derivative of the y value from Figure 3-9
Figure 3-11. The reconstructed $F_{\text{even}}(z)$ on a PS and PMMA surface and the hybrid fit for modulus calculation.

Figure 3-12. AFM height image showing the 25 grid spots on the PMMA surface.
Figure 3-13. 25 reconstructed $F_{even}(z)$ curves overlayed on top of each other
CHAPTER 4
EXPERIMENTAL DETAILS AND APPLICATIONS OF THE NANOSCALE MODULUS MEASUREMENT

Overview

Force measurements with the atomic force microscope have been well established by using contact mode\(^3\). This method can provide much important information about the tip-sample adhesion as well as the physical properties of the sample itself.

Tapping mode AFM is one of the dynamic AFM techniques developed for operation in air or liquid\(^47\). The tip sample interaction in tapping mode AFM only happens in a fraction of the total measurement time and thus it is considered gentler for sample measurement than contact mode\(^48\). In addition, the cantilever stiffness is much higher than that in contact mode and it can overcome the snap-in problem while maintaining high sensitivity. Many efforts were aimed at relating values (amplitude and phase) measured in tapping mode AFM to physical properties of the materials underneath the probe tip\(^24,26,49\). However, due to the nonlinear nature of the tip sample interactions, the inversion from experimentally accessible values in tapping mode to tip sample interaction profiles is not straightforward.

As mentioned in previous chapter few theories were published trying to quantitatively inverse the tip-sample interactions from amplitude and phase value in tapping mode AFM. These theories showed decent reconstructions numerically on a Lennard Jones type of potential or simulated DMT tip sample interaction, but no isolated physical properties of the sample materials were ever obtained. From previous chapter we were able to obtain the tip sample interaction force on solvent cast PS or PMMA surface by inversing the amplitude-phase-distance (APD) information from tapping
mode ramping and from the interaction force we measured the effect sample surface modulus within 15% standard error.

The APD curve is the raw data for any inversing theory and its quality is crucial for an accurate tip sample surface interaction reconstruction. Although in principle any APD curve with a ramping of the tapping tip can be used in our method to provide information of tip sample interactions, we found that proper experimental settings during the APD measurement were the determining factor for the reliability and the accuracy of the reconstructed interactions.

In this chapter, we present a detailed study of the effect of experiment settings on the quality of the force measurements by tapping mode AFM and provide a few example studies on a polymer surface using the inversion method.

**Materials and Methods**

Polystyrene and Poly(methyl methacrylate) were purchased from Acros and used without purification. The average molecular weight of PS is 280,000 g per mole and the average MW of the PMMA is 100,000 g per mole. Kraton 1101, which is a poly(styrene-b-butadiene-b-styrene) block copolymer with a 30% styrene weight percent, was purchased from Kraton Performance Polymers. 150 mm p doped Silica wafers were purchased from siliconwafer.org.

The silicon wafer surfaces were prepared as followed. A small crack was introduced at the edge of the silicon wafer’s flat side using a diamond tip. The wafer was fractured along the crack with a small bend. The crack can propagate through the silicon’s crystal plane and an atomically flat surface free from any contamination can be obtained. The surface was used within 2 hours after it was made. The PS and PMMA thin films were spin coated on a small piece of silica wafer at 3000 rpm from a 0.5 wt %
solution of toluene. The surfaces were then annealed at 120 °C for 12 hours in vacuum. The roughness of the prepared surfaces had a RMS roughness around 0.2 nm measured from the tapping mode height image. The Kraton surface was made by casting Kraton toluene solution with a 0.1 wt % concentration onto glass slide and letting the toluene evaporate slowly in a petri dish sealed by parafilm for 24 hours. Tapping mode AFM was performed at room temperature in air using a DIMENSION 3100 with a NanoScope V (Digital Instruments). A TESP cantilever from Bruker was used for all the measurements and a tip radius of 10 nm was used for reconstruction. The spring constant of the cantilever was determined using Sader’s method. The free resonance $f_0$ of the cantilever and the quality factor was calculated by fitting the frequency sweep curves from 0.995 $f_0$ to 1.005 $f_0$ measured 100 nm above the sample surface to a Lorentz oscillator model.

**Results and Discussion**

**From Raw ADP Data to Force Interactions**

An example of how the data was transformed from raw ADP data to force interactions on an ADP ramp on fresh cleaved silicon wafer surface is discussed below. Figure 4-1 shows the raw amplitude (A) and phase (P) data as a function of cantilever height $Z$.

The first step is to calculate nearest tip sample separation distance $D$ by $D = Z - A$. The zero point of $Z$ is arbitrarily defined during the measurement and thus both $Z$ and $D$ have an arbitrarily shift. As will be shown later, such a shift has no impact on the reconstructed forces. The next important step is to calculate the $y$ value from the ADP data sets using the left hand side of equation 3-4. Remember from chapter 3 that the $y$
value corresponds to the integral of the governing integral shown in equation 3-4. The corresponding y vs. D plot is shown in Figure 4-2. Next, the D vs. y plot is divided into a few regions by determining the local minimum on the dy/dD, which can be clearly identified in Figure 4-3. In this example, we found it was enough to just break the interaction force into two separated regions at D=-17.13 nm and each region of the interaction force was approximated by a Chebyshev expansions series shown in equation 3-8. The Chebyshev expansions series relates to the y value following equation 3-9 and the coefficients of the Chebyshev expansions were obtained by fitting the value calculated from the right side of equation 3-9 to its corresponding y value. The fit is shown in Figure 4-4 with the blue line as the y value, the red line as the first region of the Chebyshev fit to the y value and the green line as the second region of the Chebyshev fit to the y value. Please note that here the second region did not extend to the end of the y value and the reason for this will be discussed in detail in the following section. Finally with the coefficient of the Chebyshev expansions of both regions solved, the reconstructed force was calculated shown in Figure 4-5.

The key step here is the calculation of the coefficient of Chebyshev expansions from the y values and thus the quality of the D vs. y plot in Figure 4-2 is very important for the resulting reconstruction and worth careful investigation.

The Spacing in D

First let take a close look at D in Figure 4-6 which is the same as Figure 4-5 but plotted as individual data points rather than a smooth line. We can see the spacing between D is not linear at all. During the attractive region, the spacing in D is very small while once in the repulsive region, the spacing in D drastically decreased first and then become high again. Apparently the smaller the spacing in D, the higher the resolution of
reconstructed interaction forces. An ideal data set of ADP curve will have an equally spaced D so that the reconstructed force has the same resolution across the whole tip sample interaction range. Recall that D is the nearest tip sample interaction at a given cantilever height and calculated as D=Z-A. We have total control over the Z through the z direction piezo movement of the AFM. However, the amplitude A is a measured experimental response depending on the tip sample interaction and thus we have no direct control of D behavior during an ADP curve experiment. Luckily if the experiment setup was chosen properly as will be shown in the following sections, it is still possible to obtain high resolution throughout the interaction range.

**Setpoint and Resolution Limit**

Now let’s look at how the D changes as the tip getting closer to sample surface. Figure 4-7 shows the setpoint vs. the tip sample distance D on the same sample from previous section. The setpoint can be considered as normalized amplitude and is defined as the ratio of the tip vibration amplitude in the presence tip sample interaction to the free amplitude when the tip and sample is far away. The setpoint vs. phase value is shown in Figure 4-8 for reference.

Although the phase continue to changes as the setpoint decreases, the changes in tip sample distance D is rather limited once the setpoint approaches less than around 0.8. The maximum D variation below the setpoint 0.8 was around only 0.3 nm and the noise floor level in D is about 0.1nm which can be seen in the zoomed in region in Figure 4-7. In other words, the majority of changes in D during ramping happens in the region before the setpoint becomes smaller than 0.8 and the changes in D in the region with a setpoint less than 0.8 can’t be resolved very accurately.
In addition, as can be seen in last 0.5 nm of the tip sample distance in Figure 4-2, the very slow changes in $D$ correspond to a very sharp change in $y$. Recall that the noise floor level is about 0.1 nm so a small error in $D$ will lead to a large mismatch in $y$. As a result, the data set from this region is not suitable for reconstruction.

Figure 4-9 shows the same plot as in Figure 4-4 except here the whole range of $D$ was used for the fit. The fit is quite poor, especially for the last 0.5nm in $D$.

Figure 4-10 show the corresponding reconstructed tip sample interaction using the coefficient of the Chebyshev expansions calculated from Figure 4-9. Compared with Figure 4-5, the reconstructed curve would be very smooth if the last potion of the data set was discarded. If the whole data set was used, the added 0.5nm data in $D$ would fail to provide any useful information due to the large uncertainty but would actually reduce the overall smoothness of the reconstructed force region. Here less is more.

**The Amplitude Jump in the Ramp Process and How to Avoid it**

The ADP curve is obtained by recording the changes in the tip vibration amplitude and phase while reducing the cantilever height. It has been both experimentally and theoretically shown that in the AM AFM the ADP curve can experience a sudden increase in amplitude due to the dual stability of the oscillation states as discussed in Chapter 2. Since the $D=Z-A$, a sudden increase in amplitude will translate into a sudden decrease in the tip sample distance. An example of such ADP curve and its corresponding $Sp$ vs. $D$ plot is already shown in Figure 1-4. The data spacing in $D$ is greatly reduced during the jump, which means much reduced resolution in the corresponding region. Unfortunately, the jump generally corresponds to the tip moving from attractive region into the repulsive region and the skipped distance carries important interaction information on the tip sample interaction transition. Once in the
repulsive region, the tip has already passed the region with the most changes in the tip indentation and the subsequent ADP cannot provide a large enough change in D for useful reconstruction as discussed in previous section.

For tapping mode imaging, the driving frequency is normally kept slightly lower than the resonance frequency of the cantilever so that it will stay in the repulsive region for the whole image time. Similarly for the ADP curve, by making the driving frequency slightly slower than the resonance frequency of the cantilever, the jump in the ADP curve can be suppressed. Hölscher et. al. explained the reason behind the jump in the ADP curve by plotting the frequency(f_d) vs. amplitude(A) curves at different cantilever heights^{50}. They showed that the jump is due the change of the shape of the resonance frequency vs amplitude curve.

The frequency amplitude relationship in the AM AFM can be described by Equation 4-1,

$$\left(\frac{f_d}{f_0}\right)^2 = 1 - I_+ - \frac{1}{2Q^2} \pm \sqrt{\frac{1}{4Q^4} - \frac{1 - I_+}{Q^2} + \left(\frac{A_0}{QA}\right)^2} \quad (4 - 1)$$

where Q is the quality factor, f_0 the resonance frequency, and I_+ is the integral shown in equation 3-10 in the previous chapter. Assuming an interaction force profile detailed in the DMT model in previous chapter, the f_d vs. A plots as the cantilever height decreased were overlaid in Figure 4-11. The free amplitude is set to 10 nm and plots with the cantilever height 11,10.2,10,9.4,9.2 and 8.5 were shown.

During the ADP ramp, the cantilever motion will pass through all the f_d vs. A at the driving frequency, which correspond to a vertical line at x=f_{drive}. Following the same argument of Hölscher, if this line is a tangent for any of the plot it travels on, the ADP curve will experience a jump. The attractive force will bend the curve towards the lower
frequency while the repulsive force will bend the curve towards the higher frequency. Their combined effect means the vertical line can tangent the \( f_d \) vs. A plot either at lower frequency or higher. As a result, only the range of driving frequency in the between the two horizontal lines will be free of any jumps. Apparently in Figure 4-11 the stable frequency window is quite narrow.

During measurement on a real sample surface, the interaction force is unknown and thus it is not possible to draw a \( f_d \) vs. A overlay plot to determine the proper driving frequency before measurement. In addition, the tip sample interaction force will have small variations due to thermal fluctuations of the both the cantilever and the sample, scanner drift and environmental vibration. All these noises will effectively squeeze the free-of-jump driving frequency range and even make it impossible to obtain results free of jumps in the ADP curve. Luckily, the free amplitude \( A_0 \) of the cantilever motion is another parameter that can be varied for a more robust ADP curve. If the free amplitude \( A_0 \) is increased, the cantilever will have a higher restoring force, the tip sample interaction force will become relatively smaller, and the tip motion will become more stable. Figure 4-12 shows a \( f_d \) vs. A overlay plot calculated using the sample interaction force but the free amplitude \( A_0 \) is 40 nm four times the free amplitude in Figure 4-11 obtained by increasing the driving voltage of the piezo. We can see the higher free amplitude effectively zooms out the \( f_d \) vs.A curve with the amount of the distortion from tip sample interaction unchanged and the driving frequency range free of jumps becomes much wider.

**Experimental Results on Better ADP Curve for Tip Sample Force Reconstruction**

We tested the theory in the previous section on a PS thin film. The film was prepared from spin coating 0.1 wt% PS in toluene solution on a Si. Figures 4-13 to 4-16
show the typical ADP curve obtained at a random spot of the PS film with free amplitude of ~15nm and four different driving frequencies: $f_0+50$hz, $f_0-50$hz and $f_0-100$Hz where $f_0$ is the free resonance frequency of the cantilever. There’s no jumps in the $f_0+50$ hz but the cantilever stayed at a low amplitude state throughout the whole ADP curve which means the tip never indented very deep into the sample surface.

At $f_0$ driving frequency, jumps are apparent. At $f_0-50$ hz, the jumps were suppressed and the region jump happens for $f=f_0$ changes into a flat region. At $f_0-100$Hz, the jump occurs almost upon tip sample interaction.

A closer look the ADP curve in at Figure 4-15 shows that although there’s no apparent jump in the amplitude, the phase plot is quite noisy, as if the probe is struggling between a high phase value state to a low phase value state. Figure 4-17 shows the ADP curve obtained at $f=f_0-50$hz and a free amplitude ~40nm. A higher amplitude and proper selected driving frequency not only kept away the jump but also greatly suppressed noise in the ADP curve.

To prove the improved quality of the single ADP curve shown here is not due to luck, a systematic study of the noise on the ADP curves obtained at different driving frequency and amplitude were carried out on the Kraton thin film sample. The AM AFM height and phase image of the corresponding film is shown in Figure 4-18. Because of the large mechanical property difference between the two phases and small separation distance between the two phases, any slight drift in the x-y direction might disturb the cantilever state.

The driving frequencies selected were $f_0$, $f_0-50$ and $f_0-100$. Here the $f_0+$ range was omitted because the ADP curves tend to stick in the attractive region, unable to provide
enough data points on the mechanical properties of the sample. The free amplitudes were chosen at 10, 20, and 45 nm. So a total of 9 experimental conditions were selected. A fixed sample area of 1 micrometer by micrometer was used during the whole experiment. At each specific experiment setting, 25 ADP curves were obtained on a 5 by 5 grid, with a grid distance of 11 nm. The phase curves, which tend to be noisier than amplitude curves, were used to estimate the noise of the ADP curves. For each single phase curve, a smooth version was calculated using wavelet denoising with a very high threshold so that the smooth version is free from any kind of noise. Please note the smooth version is not suitable for force reconstruction because signal details could be filtered out due to the high threshold used. The noise level for that single phase curve is then taken as the mean value of the absolute difference between the raw phase values to the smooth the version. The noise level for the each experiment setting is taken as the average value of the 25 noise levels of all the 25 ADP curves taken at that experimental condition. Figure 4-19 shows the results of the noise level at different experimental settings. The $f = f_0 - 100$ and $A_0 = 40$ nm were not included due to jumps. Clearly the experimental setting resulting in the lowest noise level was obtained at the highest driving amplitude with the driving frequency at $f_0 = 50$ Hz. This result clearly confirmed the previous discussion.

**The Reconstructed Force and the Modulus Calculation Process**

With the ADP curve free of jumps and a low noise level, we can finally obtain reconstructed tip sample interaction forces. In the previous chapter we mentioned that the obtained reconstructed tip sample interaction forces were fit against the MD model to calculate the modulus. Here we will have a detailed discussion on how to obtain useful information from the attractive and repulsive regions with different models.
The reconstructed tip sample interaction force is the average tip-sample interaction of approaches and retractions during one tip oscillating cycle and it is defined in chapter 3 as $F_{even}$, which is closely related to the conservative part of the interactions force. However, the $F_{even}$ is not always the same as the conservative interactions and the nature and origin of the forces during the interaction must be understood before any model is applied to the reconstructed force. A very good discussion on the $F_{even}$ is given by Sader $^{22}$.

$F_{even}$ can be separated into two regions where the repulsive force kicks in and treated separate. An example of the reconstructed force on a PS film is shown in Figure 4-20 with the repulsive region drawn in red. Before the tip comes into contact with the sample surface, it will experience long range attractive forces (e.g. van der Waals forces), capillary forces and surface hysteresis (e.g. the difference in the approach and retract interaction in JKR model) $^{51}$. All these interactions will contribute to the reconstructed attractive region of $F_{even}$ and the complicated nature of these interactions makes it difficult to model the attractive region of $F_{even}$ with a single type of attractive model.

On the other hand, the analysis of the repulsive region is relatively simpler than the attractive region. The viscoelastic energy dissipation on a polymer surface can be modeled as an odd function of tip speed and thus the $F_{even}$ in the repulsive region can be considered as equivalent to the conservative indentation force $^{26}$. Once the tip is in contact with the sample surface, we can use the knowledge of contact mechanism to
help us model the repulsive interaction and obtain the sample surface’s mechanical properties.

The simplest approach is to fit the repulsive region using the DMT model and the fitting result is shown in Figure 4-21. The DMT fit captured the overall behavior of the reconstructed force at first glance but showed significant discrepancy at the very beginning of the repulsive force region. Such lack of fit is an indication that the DMT model is not always the best model describing the tip sample interactions forces. In fact, as summarized by Unertl, in the AFM force measurement most of the time the tip sample interactions lie somewhere between the DMT and JKR model.$^{34}$

As a result, the MD model was used, which covers the whole range from the DMT to JKR contact model as discussed in Chapter 2. We followed the detailed fitting procedure proposed by Pietrement et al.$^{40}$ The fitted result is shown in Figure 4-22, which shows an excellent fitting result. From the fitting parameter, the effective surface modulus of that spot was calculated to be 2.68 GPa. In addition, the elasticity parameter $\lambda$ calculated from the fit is around 2, very close to the JKR model, which explained the unsatisfactory fit from the DMT model.

In summary, the repulsive region of the reconstructed can be used to find the effective surface modulus of the sample surface and the nature of the tip sample contact by fitting it against the MD model. The attractive region is too complex for a straightforward analysis.

**Application on PS PMMA Blend Thin Film**

In this section, we put the theory and experimental consideration into practice and show the applications on the PS and PMMA blend thin film.
The PS and PMMA blends are frequently used in thin film experiments and the film surface morphology of the blend is processing dependent. These properties make the PS PMMA blend thin film a good model system for the application demonstrations of the AM AFM force measurement method.

It is shown that if the PS PMMA solution was spun casted on a hydrophilic surface such as the si wafer, the PS and PMMA will laterally phase separated with one phase protrude higher than the other depending on their relative ability to retain the solvent during the spinning coating procedure\(^{52,53}\). If annealed above both their Tg toward thermodynamic equilibrium, PMMA will wet the hydrophilic substrate while none of the polymer will wet the other. The final surface morphology is PS droplet on top of a PMMA layer with a large size distribution ranging from a few nanometers to a few micrometers\(^{54}\).

Figure 4-23 shows both the height and phase images of an annealed blend film. The film was first spun casted from a 1 wt % toluene solution with equal weight ratio of PS and PMMA at 2000 rpm and annealed at 170 °C for 7 days. The morphology of the annealed surface was PS droplet on top of PMMA layer due to high annealing temperature and long annealing time and thus the white protruding droplet in the height imaging should be PS. In the phase image, PS region has a smaller phase value than the bottom PMMA layer which can be attributed to the lower modulus of PS than PMMA. In addition, both PS and PMMA phase imaging is not uniform, indicating the annealing process was not complete.

Without established reference, it is not straight forward to assigned phases. Some authors used selected dissolution to investigate the phase composition\(^{53,55,56}\). Using the
force measurement developed in this dissertation, it is possible to tell PS from PMMA directly from their modulus. In both PS and PMMA region, APD curves were obtained on a 5 by 5 grids covering 50 nm by 50 nm area and the modulus calculation of corresponding area were performed. The overlay of the 50 reconstructed forces was shown in Figure 4-24, where the red curves were the reconstructed forces from brighter area in the height image while the blue curves were the reconstructed forces from darker area in the height image. The steeper blue curves indicated that the darker area had a higher modulus. The calculated modulus for the red curves is 2.3±0.7 GPa while for the blue curves is 3.8±0.8GPa. From the modulus we can easily assign that the area where blue curves were taken is the PMMA region while the area corresponding to the red curves were PS, which agrees well the established theory on the morphology of annealed PS PMMA blend. The spread of the modulus value is somewhat larger than neat PS or PMMA film, which is not surprising, since the surface of the blend is not as homogenous even though only a very small area of each phase were probed.

**Current Limitations of the Method**

It is tempting to expand the applications of the modulus measurement method as an imaging tool so that one can obtain a modulus imaging. However, a few remaining obstacles needed to be overcome to achieve this goal. Currently, the APD curves needed to be somewhat ideal in the sense that the transition from noncontact to contact must be smooth enough. Although careful efforts were made as described in previous sections to make sure the noise in APD curves is low, when different surface spot with different compositions were imaged at the same time, the stable operation window will become even narrower.
In addition, for imaging purpose, the number of obtained ADP curves will be too high for manual processing and all the processing steps from ADP curves to the final modulus values needed to be automated through programming. However, due to the potential difference in the underlying tip sample interactions, there will be subtle difference in how the raw data can be best processed. For example, if the noise in the raw data is low, the denoising threshold can be lowered so that no interaction details will be filtered out. We performed such attempt on Kraton (PS-b-PB-b-PS) thin film trying to mapping out the modulus on a 20 by 20 grid covering 100nm by 100nm area. The whole data processing was automated. However, only about half of the 400 APD curves were properly reconstructed and can be used for modulus calculation. Careful inspection of the rest of the APD curves revealed that during the denoising process, error was introduced to the D value around the noncontact to contact transitions. Manually fine tune the denoising process can help the problem. However, for a fully automated process, we believe a better denoising algorithm is needed.

Finally, the modulus calculation process from the reconstructed force assumed a homogenous sample surface. For modulus mapping on blocky polymers, due to the small size of each phase involved, the obtained modulus should not be considered as the modulus of the material in contact with the tip during each of the APD curve measurement. Only if the contact model takes into account of the nanostructure of the sample, can the modulus of each phase be accurately calculated.
Figure 4-1. Raw amplitude and phase data on fresh cleaved silicon wafer surface

Figure 4-2. Y value calculated from raw data for the reconstruction
Figure 4-3. The derivative of y value, the lowest point defines the separation of the two regions.
Figure 4-4. The fitting of Chebyshev expansions to the y value
Figure 4-5. The reconstructed interaction force
Figure 4-6. The individual data points of the reconstructed interaction force
Figure 4-7. Setpoint vs. tip sample distance, the inserted in a zoom showing the details

Figure 4-8. Setpoint vs. phase
Figure 4-9. The fitting quality greatly decreased if unnecessary data was included.
Figure 4-10. The reconstructed force if the whole data set was used
Figure 4-11. The overlaid $f_0$ vs A curves showing the stable windows for ADP curve
Figure 4-12. $F_d$ vs $A$ plot showing the same frequency range but four time the free amplitude.

Figure 4-13. ADP curve trapped in the attractive region, $f = f_0 + 50\text{Hz}$.
Figure 4-14. Jump from attractive to repulsive region, $f = f_0$

Figure 4-15. Jump suppressed, $f = f_0 - 50\text{hz}$, but phase is noisy

Figure 4-16. If driving frequency is too low, jump still will happen, $f = f_0 - 100\text{hz}$
Figure 4-17. Higher driving amplitude f=f0-50Hz

Figure 4-18. Tapping mode AFM height and phase image of Kraton thin film
Figure 4-19. The noise level at different test conditions. The result on the black square was not included because amplitude jump was observed during measurement.

Figure 4-20. The two regions of the reconstructed interaction forces
Figure 4-21. The DMT fit to the repulsive region
Figure 4-22. The height and phase image of the PS PMMA blend
Figure 4-23. The overlaid reconstructed force on both PS and PMMA regions
Figure 4-24. The MD fit to the repulsive region
CHAPTER 5
LONG TERM CREEP PREDICTION OF EPOXIES IN AN ADHESIVE ANCHOR

Project Overview

On July 10, 2006, in the Interstate 90 connector tunnel in Boston, a total of 26 tons of suspended concrete ceiling fell from the tunnel roof and fell onto a passenger car, killing the passenger in the right-front seat. The cause of the accident was determined to be excessive creep of the epoxy used in the adhesive anchors. As part of the research project funded by National Cooperative Highway Research Program (NCHRP) to investigate the long-term performance of epoxy adhesive anchor systems, the isolated creep behavior of two different adhesives from two different manufactures was measured. These adhesives were all approved by ICC-ES AC308 for use in concrete and masonry elements. Their creep behaviors were compared to the displacement of adhesive anchor displacement under constant load and an interesting correlation was observed. In addition, an accelerated testing method performed so that the long term creep behavior of the adhesive could be predicted from short term experiments.

Background

Epoxies in Adhesive Anchors

One of the well-established uses of epoxy resin are applications in sustained load structures and adhesive anchor is one of these structures in which epoxy acts both as a load bearing materials and adhesive. Figure 5-1 shows the configuration of an adhesive anchor and its load transfer mechanism. Direct tensile pull on the threaded steel rod were transferred through the threads to the shear of epoxy. Such structures’ stability and safety over their service life time is very critical, yet due to the viscoelastic nature of
the epoxy resin, the strain of epoxy resin due to continuous stresses will increase overtime. According to the Big Dg ceiling collapse accident report, 135 out of the 446 remaining anchors (after the accident) showed displacement ranging from 0.1 inches to 1 inches, out of a total thread length of 5 inches about 7 years after installation.

The current creep test method for adhesive product approval as load bearing materials is a very simple and conservative method. The adhesive anchor is subjected to 40% of its ultimate strength measured by a static test and the load is sustained for 1000 hours. The displacement readings are taken every hour for the first six hours, and then daily for the remainder of the test. The displacement vs. time data is then fitted to a log function and extrapolated to 600 days. If the predicted displacement at 600 days is lower than the mean displacement at maximum load during tensile test, the product is rejected. In fact some products have to lower their specific maximum strength so that the product can pass the test at a lower load.

**The Accelerated Creep Test of Epoxy**

The compliance of a polymer is defined as \( J = \text{strain/stress} \). As a viscoelastic material, a polymer will show a time dependent deformation under load and thus \( J \) is a function of time. Once the function \( J \) is known, the time dependent creep response of the epoxy can be obtained. Unfortunately, \( J \) is not always a unique function of time for an epoxy. For a polymer, its rheology behavior can be a function of time, temperature, stress and strain\(^{58-60}\). The multi-variable dependent behavior makes the prediction of a material’s performance in engineering application complicated. In addition, the service life time of the load bearing epoxy generally is expected to be more than a few years and it is neither economical nor practical to test their performance over their entire service time. Many theoretical and empirical efforts were made to elucidate the
compliance’s dependence on all those factors\textsuperscript{61-66}. The connection of time to other factors are of great practical importance because the knowledge of such connections makes it possible to predict the long term behavior of the material from short term testing done by varying the other factors.

The connection between time and temperature is best understood, supported by the time-temperature superposition principle\textsuperscript{58}. The time-temperature superposition principle states that the time response of a material at different temperature can be shifted in the time scale by a shift factor $a_T$ if the underlying molecular motions for the time response at different temperature share the same mechanism and change in temperature only affects the corresponding response speed. The shift factor $a_T$ depends on how the underlying mechanism is accelerated by temperature. For a polymer in the temperature range from its glass transition temperature $T_g$ to $T_g +100$, most polymers have a Williams-Landel-Ferry (WLT) type of behavior\textsuperscript{67}. There are also reports showing acceleration behaviors follow an Arrhenius type of behavior at temperature below $T_g$\textsuperscript{68}. A practical approach to obtain the shift factor regardless the underlying mechanism is to shift the response in the time domain manually so that the overlapped region due to the shift of the curve agrees with each other.

As a result, the two creep tests done at different temperatures can be shifted to provide information over a wider time scale about the tested materials. Similarly, if the tests were conducted over a range of temperatures, by shifting these tests in the time scale to match all the equivalent time-temperature regions, a master curve can be generated, which can provide information about the materials at a time scale not accessible if measured only at one temperature. It is natural to use the time temperature
superposition principle to predict the long term creep performance through short term tests. One such example is shown in Figure 5-2.

When the strain is below a certain point depending on the polymer the time temperature superposition principle works well and this strain range is called the linear viscoelastic range of the material. However, since the time temperature superposition principle only relates the temperature to time and if the strain or stress is large enough to change the speed of the underlying molecular motion mechanism or even alter the mechanism, the predicted time response from only using the temperature superposition principle will not be accurate. A few groups tried to address this issue by assuming no changes in the underlying mechanism and the stress or strain only altered the speed. Using such an approach, a stress or strain shift factor can also be introduced. An example of stress time superposition is shown in Figure 5-3.

**Experiment and Method**

The two adhesives used in this study were from two different companies and will be addressed as adhesive A and B. Both of them comes with two parts and were dispensed through an injection mixture tubing system. Adhesive A is an amine blend cured Bisphenol A epoxy resin. The adhesive B is a blend of Bisphenol A epoxy resin and Bisphenol F epoxy resin cured with amine hardeners and quartz filler.

The curing of the adhesives was set to mimic the adhesive thermal history for the real adhesive anchor system. All the adhesives were demolded after the manufacturer’s specific curing time and stored in room temperature. After a total of 7 days of curing at room temperature, the adhesive samples were transferred into the environmental chamber for conditioning for 24 hours before any testing.
The adhesives were first characterized by DSC to determine their $T_g$ and degree of crosslinking. The $T_g$ was calculated by the software while the degree of crosslink was calculated as the ratio of the residual exothermal peak of cured adhesive to the total exothermal peak of just mixed adhesive. In addition, the average tensile strength of the adhesives were tested in 110 °F (equal to 43.3 °C) in a INSTRON with an oven attached.

All the long term creep tests were done in a 12’ by 12’ by 8’ tall Cincinnati Sub-Zero Model # WM-STH-1152-2-H/AC Walk-In Stability Chamber (Figure 5-4) to condition and test at the elevated testing temperature of 110°F (43.3 °C) +10°F/-0°F and below 40% relative humidity. The test temperature is chosen at the maximum temperature any adhesive anchor will be exposed to in a high way.

The long-term creep tests were done on custom built frames (shown in Figure 5-5). A eye hook with an adjustable height on the top is used to sustain the total load on the sample. The load is applied to the sample through a 10 to 1 ratio lever arm in the bottom. The self-weight of the level arm results in around 80 lbs of base load on the sample and more weight can be added through the pole on the end of the lever arm. The long term creep samples were first tightly clamped on two ends by two fixtures and the samples were then loaded into the test frames by passing a steel thread through the hook and the two holes in the fixture for both fixtures. During loading, the upper eye hook’s height was adjusted so that the level arm was horizontal. As the long term creep elongates during creep, the level arm will gradually lean downwards. The load on the adhesive samples to the weight added in the pole in lever arm was calibrated by using a load cell instead of the adhesive sample. The four different load levels of each adhesive
were tested and each level had three replicas. The load levels were 35%, 45%, 55% and 75% of the average strength of the sample tested by tensile test.

The long term creep samples were cast into pre-made silicone molds directly from the tube. Due to the viscosity difference between the three adhesives, there’s slight difference in preparing the smooth surface that's face up with no contact of the silicone mold. Adhesives A and B were allowed to overfill the mold and then a razor blade was used to remove excessive adhesive, leaving a smooth surface by moving the blade perpendicular to the length of the sample in one pass. Later it was decided that such a procedure resulted in a too rough a surface for adhesive A and the procedure was modified. Once overfilled, a piece of glass was pressed against the mold to squeeze the excessive adhesive out. The glass was detached after the sample was cured. Adhesive A was too sticky for any overfill-squeeze processing. Luckily it was found that adhesive A will slowly flow before gelation and the final procedure for making adhesive A was to carefully control the amount of the adhesive injected into the mold and let the adhesive itself flow and form a smooth free surface.

The creep of the dogbone sample was measured with strain gauges. All strain gauges were purchased from Micro-Measurement. The gauge designation is C2A-XX-250LW-350 for adhesive A while adhesive B used EP-08-250-BF-350. Both types of strain gauges had an initial resistance of 350 ohm and a gauge factor slightly larger than 2 (2.09 for B and 2.12 for A). The difference is that the strain gauge used for the adhesive can detect strain up to 20% while for A the strain gauge had a limit of 3%. The strain gauge was attached to the degreased and polished dogbone along the strain direction using the M-bond 10 adhesive from Micro-Measurement. The M-bond 10
adhesive was allowed to cure in the test chamber for two hours before the dogbone specimens were loaded. The resistance change of the strain gauge was measured through the built in quarter bridge of a National Instruments NI 9205 modules and the data were acquired and processed by Labview.

The dynamic shear rheology (DSR) tests were performed on a TA instruments AR-EX2000 with a rectangular torsional grip and an environmental test chamber (ETC). The DSR specimens are rectangular thin sheets with thickness ranging around 1.00 mm, width around 9 mm and length around 50 mm. The uniformity of the thickness of the specimen is very important for accuracy of the measurement and every effort was made to make sure the sample thickness variation was within ±0.02 mm throughout the sample length. A thin sheet were first made by casting the adhesive onto an aluminum plate and placing spacers of 1.00 mm thickness around edges of the plates. Then another aluminum plate was put on top of adhesive and the top plate was pressed to thin out the adhesive. Once the adhesive sheet was cured, DSR specimens were cut into small rectangular strips by a precision diamond saw.

Results and Discussion

The first set of experiment was a temperature ramp at a speed of 5 degrees per minutes at 1 Hz on DSR and the results of sample A and B are shown in Figures 5-6 and 5-7. Both adhesives displayed a plateau in their storage modulus $G'$ at a temperature above their Tg, which indicates a crosslinked system. A narrower half width of the tan delta peak in sample A suggested a more homogenous crosslink network.

Figures 5-8 and 5-9 plot all the obtained strain vs. time plots of sample A and B obtained through the long term creep test. Because of the different stress levels, the strain plots are scattered. Normalizing the entire strain plot according to their stress, the
compliance vs. time plots are shown in Figures 5-10 and 5-11. The majority of the compliance plots of sample A overlap with each other and is a good indication that time temperature superposition should work for sample A. For Sample B, the compliance curves at different stress level differ from each other which mean the creep rate’s dependence on the stress level is nonlinear.

Figure 5-12 is the log-log plots of the short term creep response of adhesive A obtained through DSR tests at different temperatures and Figure 5-13 is the shifted creep response master curve at 43 °C. The shift was done by the built-in TTS processing function of the DSR instrument. Very good agreement between the overlapping region of the shifted curves shows that the time temperature superposition is valid here.

Figure 5-14 is the comparison of the long term creep compliance curve of sample A to the shifted compliance curves from the short term test. Please note that the compliance of the curves from DSR test is the shear compliance and when compared with tensile compliance obtained through long term creep test, the shear compliance was divided by $2 \times (1 + \nu)$ where $\nu$ is the Poisson’s ratio of the epoxy (taken as 0.4). They did show agreement with other at the early stage of creep but the creep predicted from DSR test grew faster than the tensile creep, which may be due to additional cure of the long term sample during the thousand hours long creep test. To test this hypothesis, the DSR samples were allowed to cure in 50 °C for 2 days and the master curves were constructed again shown in Figure 5-15. The discrepancy in the master curves and the long term creep compliance happened 100 hours later than the previous result, which confirms the effect of the additional curing.
Due to the nonlinear behavior observed during the long term creep test of sample B, the short term creep curves might also be accelerated by the applied stress or the resulted strain and if the shift factors were directly obtained through shift of the creep curve, the shift factor will be coupled with the applied stress during the short term creep experiment. Since the frequency sweeps measurement can be done at very low strain level, where the nonlinear behavior’s effect is negligible in the linear viscoelastic region, the shift factor for time-temperature superposition was obtained by shifting the frequency sweeps at different temperatures. As a result, eight frequency sweeps from 0.1 Hz to 10 Hz were performed at the same temperature of the creep test with a maximum oscillation strain at 0.05% and shifted with 43 °C as the reference temperature. Using the shift factor obtained this way, the short term creep tests of sample B shown in Figure 5-16 were shifted accordingly. The result is shown in Figure 5-17.

The comparison between the compliance obtained from the long term creep test and the compliance predicted from the DSR test were shown in Figure 5-18. An apparent trend in Figure 5-18 is as the load is increased during the long term test, the compliance increases at higher speeds over time, which should be due to the accelerating of the creep mechanism due to stress.

To investigate if there’s any simple stress time superposition relation, 5 creep tests on adhesive B with shear stress ranging from 0.5, 15, 20, 25 to 35 MPa were tested on the DSR. Any further increase of the test stress resulted in the failure of the test specimen. The raw and shifted curves are shown in Figures 5-19 and 5-20. Only if the horizontal distance between the overlapping regions of two curves is a constant can
satisfactory superposition be possible. The poor matches of the shifted curve indicate that no simple time stress superposition type of relationship exists for adhesive B.

In fact the horizontal distance between any two curves is not a constant but a function of compliance. We calculated the horizontal distance between any two pair of the compliance curves in Figure 5-19 resulting in a total of $C_s^2=10$ pairs and plot against the log10 of the corresponding compliance regions. Please note that if simple stress time superposition relation existed, we would have a few horizontal lines at different height, which depend on the stress level difference. The actual result is shown in Figure 5-21. For each curve in Figure 5-21 three numbers were labeled, which indicating the stress levels of the pair of compliance curves they were calculated from (labeled beside each curve) and the difference between the two stress levels( labeled on each curve). Please note that here 0.5 MPa was treated as 10 MPa during the calculation of the stress difference so that the calculated stress difference agreed with the curves they overlapped. An interesting find is that the curves from the same stress level difference seem to fall on top of each other. In addition, curves with a greater stress level difference had greater shift factor as well.

Similar treatment was done to the long term creep compliance curves of adhesive B which was drawn in red in Figure 5-22, overlaid with the curves from Figure 5-21(the black curves). After the initial agreement of short term test, the curves from long term creep did not follow the trend of the curves from short term creep. However, if the long term compliance axis was plotted linearly, drawn blue in Figure 5-23, the log of the shift factor becomes a linear function of the compliance after a certain point in compliance!
We performed linear fit for all the plots using the data points where compliance equals $5\times 10^{-10}$ Pa$^{-1}$ and drawn in green in Figure 5-23 as well. Depending on the stress level, it takes about 2~10 hours for the compliance to reach this value. Clearly the fittings are very good for all the curves and all the green plots converge roughly to the origin of the coordinate system. The slope of each of the fit and the stress difference for each of the fit was plotted in Figure 5-24. A fairly good linear fit was obtained with R value equal 0.909 and slope=44.7. In addition, the intercept on the y axis of the linear fit is very close to origin as well. As a result, we postulate that the shift factor for adhesive B can be approximated as

$$\log_{10} a = C \times \Delta\sigma \times D$$  \[(5-1)\]

where $a$ is the shift factor, $\Delta\sigma$ is the difference in stress, $D$ is the compliance at which the shift factor is calculated and $C$ is a material dependent constant which can be calculated from the slope of the red line of Figure 5-24.

Since the shift factor can be regarded as the viscosity ratio for two tests, from equation 5-1 it can be seen that the viscosity is proportional to exp(stress), which indicating an Eyring type of viscosity stress relationship$^{76}$. If there's no $D$ term in equation 5-1, a simple stress time superposition will be enough to describe the stress dependence of the creep behavior. Since stress time superposition assumed unchanged creep mechanism we believed the presence of $D$ term means a dependence of the underlying creep mechanism on the current state of the polymer during the creep test. The reason currently is still unknown to us but the apparent linearly relationship of the log10 of the shift factor with $D$ makes this a very interesting problem for further investigation.
Discussions and Recommendations

Time temperature superposition can be a powerful tool for accelerated test for polymer testing. However, for epoxy resins used in commercial adhesive product, due to the complexity of their formula, one should not assume time temperature superposition always work. For the adhesive A used in this study, time temperature superposition seems like a reasonable method for long term creep prediction for very short term DSR test. As for adhesive B, it was observed that the linear viscoelastic behavior was not valid and the creep behavior depend on the stress applied. Although time stress supposition method was reported to be valid for a few polymers, we found the effect of stress can be more complicated. For adhesive B, the dependence of shift factor on the stress is quite different between the long term creep test and short term DSR creep test. Nevertheless, it is found that after the creep compliance pass a certain point, the relationship between the shift factor, compliance and stress become simple and apparently followed equation 5-1. As a result, we commend the following steps to predict the long term creep behavior from a set of relative short term tests.

First construct a master compliance curve from DSR test within linear viscoelastic range for very low stress level following the steps as shown in Figures 5-16 and 5-17. The length of each DSR creep test can be as short as 30 minutes.

Second, perform DSR creep test under different stresses to see if there is any stress dependence on the compliance. If such dependence does exist, try the stress time supposition first. If worked, measured the short term creep test at desired stress level to obtain the shift factor and shift the master curve from step 1 accordingly.

If the stress temperature superposition does not work, it is still possible to predict the long term creep performance. In this case, the short term creep tests have to be run
long enough until equation 5-1 become valid, which will take about 2 to 10 hours from experience of adhesive B. With this data, one can obtained the C in equation 5-1 and combining with the master compliance curve from step 1, the long term creep performance at any stress level can be obtained. Although this is not a very short test, it is still reasonably short.

Figure 5-1. The load transfer mechanism of an adhesive anchor (after Eligehausen et. al., 2006)
Figure 5-2. An example of time temperature superposition (after Goertzen, W.K., et. al., 2006)

Figure 5-3. An example of time stress superposition (after Jazouli, Said, et. al., 2005)
Figure 5-4. The environmental chamber for the long term creep test. Photo courtesy of Todd Davis

Figure 5-5. The test frame setup for the long term creep test. Photo courtesy of Changhua Liu
Figure 5-6. The DMA test results for adhesive A

Figure 5-7. The DMA test results for adhesive B
Figure 5-8. The strain over time for long term creep of adhesive A at different load level
Figure 5-9. The strain over time for long term creep of adhesive B at different load level
Figure 5-10. The compliance over time for long term creep of adhesive A at different load level.
Figure 5-11. The compliance over time for long term creep of adhesive B at different load level.

Figure 5-12. The compliance over time for DSR test of adhesive A at different temperature.
Figure 5.13. The shifted master compliance curve for adhesive A using 43 °C as reference temperatures

Figure 5.14. The comparison between predicted compliance from DSR test and long term creep test for adhesive A
Figure 5-15. The comparison between predicted compliance from DSR test and long term creep test for adhesive A with higher curing temperature

Figure 5-16. The compliance over time for DSR test of adhesive B at different temperature
Figure 5-17. The shifted master compliance curve for adhesive B using 43 °C as reference temperatures

Figure 5-18. The comparison between predicted compliance from DSR test and long term creep test for adhesive B
Figure 5-19. The compliance over time for DSR test of adhesive B at different stresses.
Figure 5-20. The shifted master compliance curve for adhesive B using 0.5 MPa as the reference stress
Figure 5-21. The shifted factor as a function of compliance for each pair of compliance creep curves at different stresses for short term creep tests
Figure 5-22. The shifted factor as a function of compliance for each pair of compliance creep curves at different stresses for both long term (red) and short term (black) creep tests.
Figure 5-23. The shifted factor as a function of compliance for each pair of compliance creep curves at different stresses for the long term creep drawn in blue semilog plot. The linear fit of each curve was drawn in green.
Figure 5.24. The difference in stress vs. the slope of the fit for each of the plot from Figure 5.23. The red line is a linear fit to the data. $R^2 = 0.909$
CHAPTER 6
CONCLUSION AND FUTURE WORK

The viscoelastic nature of any polymer makes it impossible to characterize its mechanical property with a single value. What’s more, the recent advances in nanotechnology enable us to vary the composition of polymers in the nano-scale, which adds even more complexity for an accurate description of their mechanical properties. In this dissertation, we tried to address two aspect of this complexity. On the nano size scale and millisecond time scale, we were able to develop a robust method for measuring the nano-scale effective surface modulus based on AM AFM. On the size and time scale for long lasting load bearing structures, we measured the long and short term creep behavior of epoxies used in the adhesive anchor and investigated the relationship between creep time, temperature and stress.

The development of AFM has come a long way since its invention to meet the demand for ever more accurate measurements in nanotechnology. AM AFM is one of the most widely used AFM modes nowadays. People can use the AM AFM to look at the nano sized soft materials gently and in the same time enjoy the ease of AM AFM sample preparation process. Yet, a quantitative characterization of the soft materials in nano-scale using the same instrument for imaging has remained on the AM AFM feature wish list for years. Our method has finally made this wish a reality.

There’s still more left to explore for our quantitative AM AFM measurement. One important potential expansion is to measure bio-molecules, e.g. DNA, protein, in their native environment and this require the AM AFM to be operated in liquid. When AM AFM operates in liquid, many factors are different from in air operation and several assumptions are no longer valid. The quality factor of the cantilever decrease greatly
and the underlying interaction many change as well\textsuperscript{77}. It has been found the second eigen mode will also be excited during tip sample interaction in liquid\textsuperscript{78}. All these changes may make our method developed for AM AFM operated in air no long valid. However, there were already reports that it was possible to suppress the second eigen mode signal for liquid operation by changing the position of the laser spot on the cantilever\textsuperscript{79}. We think using similar modification to our method will allow operation in liquids.

Our investigations of the short and long term creep behavior of epoxy showed it is possible to predict the long term creep behavior of epoxy adhesive from a few short term tests for some types of adhesive resin. The results from the prediction can be used as guide for adhesive anchor approval process. In addition, we found an interesting correlation between the creep shift factor and the compliance itself. The underlying reason for this correlation can be an interesting topic for future research.
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BIOGRAPHICAL SKETCH

Changhua Liu entered University of Science and Technology of China in 2003 and earned his Bachelor of Science degree in the Department of Macromolecular Science and Engineering in 2007. He came to University of Florida in August 2007 in pursuit of a Ph.D. degree in Materials Science and Engineering and joined Dr. Elliot P. Douglas’ research group in January 2008, focusing on epoxy related researches.