SCANNING PROBE MICROSCOPY STUDY OF PSAS: RECENT DEVELOPMENTS

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Abstract

The objective of the work is to connect the near surface behavior of a model pressure sensitive adhesive with its overall adhesive performance. Measurements of the lateral force experienced by a scanning tip under small amplitude (2-20 nm) X-modulation reveal the different character of different polymeric matrices and also of the different regions at the surface of a heterogeneous adhesive. Combining the X-modulation technique with a force-distance curve measurement is found to yield a more precise and reproducible characterization. First measurements have been done on the variation in observed behavior with relative humidity.

Introduction

The objective is to better understand how the dynamic mechanical properties of the near surface region determine the performance of pressure sensitive adhesives (PSAs). It has already been demonstrated that imaging with Scanning Probe Microscopy (SPM) allows the identification of lateral segregation at the surface in inhomogeneous adhesives,1,2 and that measurement of friction force microscopy (FFM) and force-distance (F-D) curves provides laterally resolved qualitative information on the mechanical properties in the near surface region.2-3 We have also recently published4 a description of the use of a novel scanning probe technique using small amplitude lateral modulation of the tip to probe the nanomechanical properties of the surface. This approach was first suggested recently for use with other materials.5-8 By their very nature lateral modulation techniques should be better suited for capturing the properties just at the surface because they involve minimal penetration.3 It is applied here to the study of Pressure Sensitive Adhesives (PSAs) for the first time. Also we have focused on making measurements at varying humidity and refining the X-modulation technique by combining it with simultaneous measurement of a force-distance (F-d) curve, an extension which may prove useful for placing the measurements on a quantitative basis.

Experimental

Sample Materials and Preparation

Poly(ethylene propylene) (PEP) with a weight average molar mass of 244,000 g/mole and a polydispersity index of 1.7 was used as the matrix for the model adhesive blends. An n-butyl ester of abietic acid (nBEAA) was chosen as a model tackifier because its chemical structure is well known, it could be readily synthesized, and it belongs to the family of wood resin derivatives widely used in commercial tackifiers. The molecular weight and glass transition temperature of nBEAA are 358 g/mol and -45 °C, respectively. The samples were prepared by solution casting on microscope slides with film thicknesses ranging between 2 and 3 mils (50-70 μm). Samples denoted as PEP/60 and PEP/80 contained 60 and 80 wt% tackifier, respectively. PEP/60 had a homogeneous surface and the surface of
PEP/80 had domain and matrix regions, as shown in Figure 1. Measurements were also made on a silicon wafer and a cast film of polystyrene (PS) as reference samples because they are elastic. The PS glassy film was made by casting on a microscope slide a PS solution made from polymer with a molecular weight of 390,000 g/mole ($M_w/M_n = 1.05$).

**X-modulation**

X-modulation experiments were performed with the Autoprobe™ CP in lateral force microscopy mode using the signal access module. The sample was modulated laterally using the built-in piezo tube and the driving voltage and frequency were controlled using a lock-in amplifier (Stanford Research Systems, SR830 DSP). The displacement of the sample was only a few nanometers and this amplitude was calculated after calibrating the relationship between applied voltage and piezo movement. All measurements for X-modulation were done inside a glove box under controlled humidity (RH 20 % unless noted otherwise) and temperature (25 °C). In order to create an environment of enhanced, controlled RH N$_2$ gas was passed through a reservoir of hot water and then into the environmental chamber surrounding the microscope. Thirty minutes was allowed for equilibration at each humidity. Measurements at relative humidities of 23, 40, and 77% were made for the different surfaces.

A schematic of the apparatus used for the X-modulation measurements combined with force-distance curves is shown in Figure 2. The sample was modulated laterally at a frequency of 200 Hz with an amplitude of 2 to 20 nm at a linear velocity of 800-8000 nm/sec using the built-in piezo tube. Simultaneously, the sample was moved vertically toward and then away from the tip at a rate of 10-300 nm/sec using the z-piezo. The response of the cantilever to this movement of the sample is registered by monitoring the reflection of a laser beam from the back of the cantilever and into a four quadrant detector. Vertical deflection of the cantilever is quantified to deduce the normal force on the cantilever, while the lateral force at the sample surface is derived from the twisting of the cantilever. To obtain the A-B and lateral force signal with good time definition and high precision, a commercial A/D converter card was installed in the computer used for data acquisition. To obtain more specific information such as the amplitude of oscillation and phase lag of the lateral response, the lateral force signal was passed through the lock-in amplifier and then the processed signals were fed to the data acquisition software.

**Results and Discussion**

**Evaluation of Stickiness of Adhesive Surfaces using X-modulation**

Details of the X-modulation technique have been given elsewhere. With increasing forcing amplitude, the peak-to-peak amplitude of the response increases in the "stick" regime because the extent of the cantilever torsion is directly proportional to the sample displacement. When the lateral force exceeds that characteristic of the static friction, the tip starts to slip and then the lateral force reaches a constant value. This constant value is the so-called dynamic friction force, which corresponds to one half the peak-to-peak amplitude. Figure 3 compares the behaviors among the five surfaces studied. One can see the stick-slip transition on the surfaces of silicon oxide, domain of PEP/80, and PEP/60. The X-modulation responses of the matrix and domains of PEP/80 were sharply different. For the matrix regions of PEP/80 the responses were sinusoidal and the peak-to-peak amplitude increased monotonically with forcing amplitude for the entire range of forcing amplitude investigated. By contrast, on the silicon oxide surface, and on the domains of PEP/80 and on PEP/60, slip was observed at sufficiently high values of forcing amplitude. From the higher transition amplitude and lateral force, as well as the presence of the stick-slip transition itself, we conclude that the domain has both elastic and sticky characteristics. The high lateral forces observed in conventional LFM scanning images of the
matrix regions at the surface of PEP/80 are caused by deformation effects. The torque has its origin in the viscoelastic properties of the matrix, not its "stickiness". It is the domain that is actually "stickier."

**X-modulation with a Force-distance Curve**

One useful extension of the X-modulation technique is combining it with a simultaneous measurement of the force-distance curve because in this way several pieces of information are obtained simultaneously. While the adhesive force and apparent stiffness of surface can be estimated by analyzing the response of cantilever in the z-direction, analysis of the lateral response provides information on the frictional behavior and the phase lag that originates from slipping of tip or the viscoelastic properties of the sample. Data acquired during relatively fast loading (360 nm/sec) with X-modulation at 200Hz are shown in Figure 4. Four signals were captured simultaneously over a 1 second period. Vertical deflection of the cantilever(A-B) is quantified to deduce the normal force on the cantilever, while the rms lateral force, R (= \sqrt{(X^2 + Y^2)}), at the sample surface is derived from the twisting of the cantilever, where X and Y correspond to the in-phase and out-of-phase amplitudes, respectively. The average uncalibrated lateral force (expressed in volts) is calculated as

\[
F = 0.5(\text{Peak to Peak}) = \sqrt{2 \cdot \sqrt{(X^2 + Y^2)}}
\]

and the phase angle is given by \(\tan^{-1}(Y/X)\).

The lateral modulation of the sample manifests itself in the high frequency oscillations seen superposed on a force vs. time curve which is an analog of a more conventional force-distance curve. On the left side of the graph the trace corresponds to the approach of the sample to the tip before contact. The tip jumps into contact with the sample at the point where the force suddenly increases. Then the curve begins to move down. This corresponds to the increase in normal force as the tip penetrates into the sample. So the slope of this curve is determined by the rate of the z-modulation and the compliance of the material, the slope increasing with decreasing compliance if the compliance of the sample is less than that of the cantilever. The lowest point in the curve corresponds to the end of the loading process and beginning of the unloading process. For this sample we find that the unloading also results in a linear force vs. time trace, but the trace rises above the zero force level, which means that the tip adheres for some time to the surface. Once the force attempting to restore the cantilever to its rest position exceeds the adhesion force the tip snaps off the surface and the force returns to the same value (zero) as before contact. Although the oscillations of the LFM signal can be recorded clearly for a high loading speed experiment, the processed signal, R, shows a delay which is an artifact of the limited acquisition speed, which makes it difficult to analyze the results precisely.

If one is willing to sacrifice the resolution of the detail in the oscillating LFM signal, artifact-free processed signals can be captured by reducing the loading speed to 10 nm/sec. An Ultralever™ B cantilever (normal spring constant=0.4 N/m) was used in this experiment with a forcing amplitude of 0.004V, which corresponds to a lateral displacement of the sample of 0.8nm. This is the minimum displacement for our instrumentation because we attempted to keep the tip in the stick regime during acquisition. Once slip occurs, the response is controlled by slip phenomena and the challenges in determining the surface properties from the data become even greater. Four different surfaces were studied. The first was the hard, elastic surface presented by the native oxide of a silicon wafer. A second elastic surface was that of the glassy PS film. The third surface was that of poly(ethylene propylene) (PEP). This homopolymer has been used as the polymer used as the matrix in the model adhesive. Finally, the aged PEP/60 sample was studied. This particular composition blend has been found to be the most highly adhesive in earlier AFM work in this group. The responses, summarized in Table 1,
were sharply different among the different samples.

Before discussing differences among the surfaces, three important points should be considered. First, even though the silicon wafer was selected as a type of reference sample, the results from that surface cannot be compared directly with those from the other surfaces because the behavior was of the "slip" sort, even for this smallest displacement. The high value of the phase lag is clear evidence of the slip occurring. When slip occurs the slope of the loading curve decreases with increasing tip deflection on a force distance curve and a finite phase lag will be observed, even though the material is elastic. Since R is a function of normal force, if the final load force, $F_{n,max}$, varies among samples that variation has to be accounted for before comparing values of R among samples. Here, we compare values of $R_{reduced} (= R_{max}/F_{max})$, rather than using values of $R_{max}$, where $R_{max}$ is the uncalibrated lateral rms force at the maximum load, $F_{max}$.

Finally, we have to consider the reliability of a F-d experiment using AFM as a tool for nanoindentation. An overview of nanoindentation measurements of polymers has been discussed provided by VanLangdingham. The advantage of using a commercial AFM instrument for such a measurement is the potential to combine nanoindentation with high resolution imaging capability. However, because commercial AFM systems have not been specifically designed for indentation testing, a number of instrument uncertainties severely limit their uses as a nanoindentor. Despite these limitations, successful studies of polymers have been completed by either reporting the results on a relative basis or reporting them with high uncertainties due to the use of nominal spring constants, the assumption of idealized tip shapes inherent to the Hertzian or Sneddon analysis, and the neglect of viscoelastic behavior. This assessment is exactly applicable to X-modulation. Obtaining reliable quantitative results requires calibration of all the parameters with high accuracy. However, this calibration is a non-trivial process having much higher uncertainty than for nanoindentation. Therefore, in this contribution, we focus on qualitative and relative comparisons among the different surfaces.

The responses of the PEP and PEP/60 surfaces differ sharply. The small values of stiffness and $R_{reduced}$ and high phase lag for the PEP surface may be related to the liquid-like character of its surface which results in efficient damping of the tip movement. Since we believe the aged PEP/60 surface is highly enriched in tackifier, its relatively high stiffness is reasonable. However, its very high value of R as compared to the other surfaces is intriguing. This may be explained if we postulate that the lateral movement of the tip is much more sensitive to the "stickiness" of the surface than is the z-modulation. In our earlier X-modulation study, we argued that the amplitude of the response to the oscillatory forcing function and the behavior of the "stick-slip" transition is very sensitive to the adhesive force between the tip and the sample. This adhesive force should be even more important in the experiment that combines X-modulation with the F-d curve because the final normal load increases up to 20 nN, resulting in an enhanced interaction between the tip and sample. Again, one finds that the surface of PEP/60 is "sticky".

**Humidity Effects**

The relative humidity of the environment is known to have a strong influence on adhesion and for the most rigorous exploration of adhesive surfaces using the new technique humidity must be controlled as an additional experimental parameter. Small variations in behavior with humidity were seen for the PEP surface as shown in Figure 5, where a normalized value of rms response is plotted as a function of time at three forcing amplitudes. $R_{normalized}$ is given by

$$R_{normalized} = R_{exp} \times \frac{F_{max,0.004V,RH=23}}{F_{max,exp}}.$$  

At relatively high forcing amplitude, the lateral force decreases with humidity. This is reasonable because even if no strong interaction with water is expected due to the hydrophobic character of the PEP surface, water can act as a lubricant during tip movement, which results in a reduced frictional force.
Results from an X-modulation experiment without the simultaneous F-d measurement (not shown) also exhibit the same trend.

The response of the PEP/60 surface, however, showed strong variation with humidity. Figure 6 shows the variation of $R_{\text{normalized}} = \frac{R_{\text{exp}}}{F_{\text{max,RH=23}}/F_{\text{max,exp}}}$ and normal force as a function of time for three different relative humidities. The value of $R_{\text{normalized}}$ rises rapidly upon contact initial loading and then remains roughly constant through the remainder of the trace. The rms lateral force increases substantially with humidity. We conjecture that this is due to interaction between the humidity and the tackifier. Figure 6b shows traces of the normal force with time, derived from the A-B signal. The trace changes a small amount with the humidity increase from 23 to 40%. The maximum normal force attained decreases and the sample compliance is seen to be lower at the higher humidity, as evidenced by the lower slope. Also a small curvature appears in the unloading curve. However, upon increasing the humidity to 77%, maximum force attained decreases dramatically, the time required to reach the end of the loading sequence drops and a stronger curvature appears in the unloading curve. This is because the more hydrophilic nature of the PEP/60 surface results in strong, but complicated interaction with water. The changes with humidity are presented in a summary fashion in Table 2, where values of quantitative descriptors of the behavior are tabulated. At the highest humidity (RH = 77%), the overall stiffness has dropped to around 0.06 N/m, a value similar to that of the pure PEP surface. At the same time the phase lag has increased slightly, but the value of $R_{\text{normalized}}$ has increased dramatically. It is highly likely that as a result of the different interaction at the surface, the tip penetrates more deeply into the sample in the case of the highest humidity. In that case the tip may penetrate to the “bulk” of the sample, which has a lower hardness than does the tackifier enriched surface, resulting in a smaller normal force being observed. The sides of the tip may still be in contact with the tackifier rich surface region and the condensed water layer on the surface of the sample, and this may be responsible for the higher lateral force during lateral oscillation of the sample. To move from such conjectures to solid arguments we need a more rigorous analysis to obtain values of the penetration depth and contact area. This analysis is currently underway.

Summary

The adhesion properties of model pressure sensitive adhesives have been investigated using a new protocol that enables one to evaluate the nanomechanical behavior of the near surface region by directly observing stick-slip motion. From the amplitude of oscillation and magnitude of lateral force at the transition point, qualitative differences in strength of the surface stickiness were identified. Progress has also been made toward quantifying the description of the surface properties. Due to the large uncertainties in some of the data collected with the original protocol, we have improved on the X-modulation approach by combining it with a simultaneous slow, large amplitude z-modulation typically known as a "force-distance" measurement. X-modulation data taken during the force-distance measurement are more reliable, more reproducible, and thus more sensitive to subtle changes at the surface. Using this approach, the properties of the surface of an aged PEP/60 sample were found to be much more sensitive to variations in humidity than were the properties of the homopolymer matrix by itself. Earlier results have already shown that the sample with 60wt % tackifier loading also has the most adhesive surface of those studied.
References


Acknowledgements

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**Table 1.** Key features among different surfaces.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>PEP</th>
<th>PEP/60</th>
<th>PS</th>
</tr>
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<tbody>
<tr>
<td>$F_{n,\text{max}}$ (nN)</td>
<td>9.4</td>
<td>5.8</td>
<td>20</td>
<td>35</td>
</tr>
<tr>
<td>$R_{\text{max}}$ ($V_{\text{rms}}$)</td>
<td>1.9</td>
<td>0.1</td>
<td>3.2</td>
<td>2.3</td>
</tr>
<tr>
<td>$\theta_{\text{max}}$ (deg)</td>
<td>25</td>
<td>14</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Stiffness (nN/nm)</td>
<td>0.2</td>
<td>0.07</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>$R_{\text{reduced}}$ ($V_{\text{rms}}$/nN)</td>
<td>0.2</td>
<td>0.02</td>
<td>0.2</td>
<td>0.07</td>
</tr>
</tbody>
</table>

**Table 2.** Variation in properties with relative humidity for PEP/60.

<table>
<thead>
<tr>
<th>Relative Humidity(%)</th>
<th>Pull-off Force (nN)</th>
<th>Stiffness (nN/nm)</th>
<th>$\theta_{\text{max}}$ (deg)</th>
<th>$R_{\text{normalized}}$ ($V_{\text{rms}}$)</th>
<th>Ratio ($R/R_{\text{RIP-23}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>1.4</td>
<td>0.21</td>
<td>0.8</td>
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<tr>
<td>40</td>
<td>1.1</td>
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<td>1.0</td>
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<tr>
<td>77</td>
<td>2.7</td>
<td>0.06</td>
<td>3.5</td>
<td>23</td>
<td>7.4</td>
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</tbody>
</table>
**Figure 1.** Topographic AFM images of the surfaces of three film samples: PEP homopolymer, PEP/60 and PEP/80. The images were measured in contact mode.

**Figure 2.** Schematic of the instrumentation used for characterization of the surface by X-modulation with simultaneous collection of a force-distance curve. At right is shown also the variation of the LFM signal as a function of time for this type of measurement.
Figure 3. Variation in the peak-to-peak lateral force with forcing amplitude at 200 Hz with a normal force of 10nN for the silicon oxide surface or 5nN for the homogeneous surface of PEP/60, the tackifier enriched domains of the PEP/80 sample, the matrix of the PEP/80 sample, and the homogeneous surface of the PEP homopolymer.

Figure 4. Traces vs. time of four signals captured simultaneously during a measurement combining X-modulation with a force-distance measurement with a fast loading rate (360 nm/sec).
Figure 5. Variation in the X-modulation response with a change in relative humidity from 23 to 77% for the surface of the aged PEP sample when measured using X-modulation in combination with the force-distance measurement. Results are shown for three forcing amplitudes: 0.004, 0.05, and 0.1 V.

Figure 6. a) Variation with time in normalized rms lateral force for the PEP/60 surface at three relative humidities: 23, 44, and 77%. b) Variation in normal force with time (derived from the A-B signal) for the same experiments for which data are shown in part a).