

Influence of Humidity on Surface Behavior of Pressure Sensitive Adhesives Studied Using Scanning Probe Microscopy

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The effect of humidity on the adhesive properties of a model pressure sensitive adhesive (PSA) composed of poly(ethylene propylene) (PEP) and the *n*-butyl ester of abietic acid was studied using lateral modulation (X-modulation) measurements with a scanning probe microscope. The lateral force on a probe oscillating laterally in the “stick” regime decreases slightly with increasing humidity on the hydrophobic surface of the pure polymer matrix. On the homogeneous, hydrophilic surface of the adhesive loaded with 60 wt % tackifier (PEP/60), the corresponding lateral force grows strongly with increasing humidity. To better understand how the humid environment affects the nanomechanical properties of the adhesive surface, the X-modulation technique was combined with a force–distance curve measurement to yield a more precise and reproducible characterization. The properties of the surface of an aged PEP/60 sample were much more sensitive to variations in humidity than were the properties of the homopolymer matrix by itself. A large oscillating lateral force in X-modulation and small stiffness in a force–distance curve were observed for PEP/60 at high humidity. These observations are consistent both with a model that envisions a tackifier-enriched region within 50–100 nm of the surface and with the hypothesis that at a hydrophilic surface water molecules may strongly alter the surface–tip interactions or modify the mechanical properties of the material nearest the surface.

Introduction

The measurement of material surface properties using scanning probe microscopy (SPM) is of great importance in nanotechnology. For example, friction at the nanometer length scale,^{1–6} adhesion forces on nanoscale contacts,^{7–11} and single chain dynamics of biological molecules^{12–14} have all been the subject of recent SPM study. Since these properties are very sensitive to environmental conditions, several research groups have already demonstrated the effect of humidity on both the macroscale and microscale.^{1–11} In particular, the role of humidity on adhesive force has been extensively studied, because it is clear that the formation of a capillary neck of water between the tip and surface can change the observed behavior dramati-

cally, even if the nature and extent of this effect are not well understood. In general, water-mediated interaction between tip and surface is much more complicated than the capillary force itself, because the overall interaction can involve several types of interactions including van der Waals forces, electrostatic forces, and chemical bonding.

Most work, however, has focused on the study of the capillary force or the effect of humidity on sliding friction using an elastic, hydrophilic surface like mica^{1,2,6,9,10} or silicon.^{1,3,8} Elastic, hard surfaces have been the focus because for soft materials surface deformation during contact is highly significant, making analysis of the interactions more complex. Therefore, only a few papers^{1,5} have dealt with organic materials such as self-assembled monolayers and polymers.

In this contribution, we report on the effect of humidity on adhesive properties of a model pressure-sensitive adhesive (PSA)^{15–18} for the first time. We are interested in PSAs because PSAs are typically composed of a high molecular weight elastomer and small, bulky molecules called tackifiers, and quantifying the effect of tackifier loading on the rheological and mechanical properties of the adhesive is important to understanding how the tackifier functions. Although researchers have studied the bulk properties of PSAs over the past four decades,^{19–21} the question of how the tackifier alters the adhesive behavior at the molecular level still remains.

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To study the effect of humidity on the surface behavior of PSAs, we have employed the lateral modulation (X-modulation) technique,^{22–29} while much of the previous work done on the effect of humidity on tip–surface interactions has focused on the measurement of adhesive force. Several groups have shown that there is a discontinuity in the variation of adhesive force with humidity for other sorts of surfaces.^{8–10,30} This discontinuity occurs at a relative humidity between 20 and 40% depending on the nature of the solid surface. To investigate this transition, studies have been undertaken using sum-frequency generation (SFG) vibrational spectroscopy,³⁰ scanning polarization force microscopy,⁹ and scanning probe microscopy with modified tips⁸ as well mathematical modeling.¹⁰ In attempting to explain the humidity effects observed, the authors of those studies have focused on a discussion of the capillary force. In the calculation of the capillary force, the well-known formula $F_{\text{cap}} = 4\pi\gamma R \cos \theta$ is used, where R is the radius of the sphere, γ is the surface tension of the liquid, and θ is the meniscus contact angle. However, as noted by other authors,^{8,9} two assumptions required for the use of the above equation, the treatment of γ as a constant and the condition that $R \gg r$, are not appropriate for a nanoscale contact in a high-humidity environment. Since this ideal geometry of contact may be distorted significantly for soft materials due to surface deformation, the estimation of the capillary force for polymeric surfaces using the above equation could have high uncertainties. In choosing to study humidity effects with PSAs using the X-modulation technique, we have shifted the focus away from the estimation of the capillary force, even though it is clear that the magnitude of the force still plays a role in determining the observed response. By combining X-modulation with the measurement of a force–distance curve, we will also gain access to more than one type of information with a single experiment.

The effect of humidity on the frictional force at surfaces has also been studied using lateral force microscopy (LFM).^{1,3} The results indicate that both the friction force and the friction coefficient may be very sensitive to humidity depending on the chemical nature of the sample and the interaction between tip and sample. However, the key point is that all of these studies focus on “sliding friction”. Again, if one wishes to perform this sort of study for polymeric surfaces, it should be expected that deformation effects will be important in determining the observed lateral forces, especially for highly adhesive polymeric surfaces. In our previous study,¹⁸ we demonstrated how X-modulation could identify qualitative differences in the strength of surface stickiness. In brief, the magnitude of an oscillating lateral force in the “stick regime” is very sensitive to the adhesive force between the tip and surface. In contrast, lateral forces measured during conventional line scanning (which occurs at higher

linear velocities and thus in the “slip” regime) are dominated by surface deformation, not stickiness.

The organization of this paper is as follows. First, we discuss the effect of humidity on the oscillating lateral force, measured using the X-modulation technique, at the homogeneous surfaces of the pure homopolymer, poly(ethylene propylene) (PEP), and the adhesive loaded with 60 wt % tackifier (PEP/60). We then present results from an improved method for characterizing the humidity effect in which X-modulation is combined with a force–distance curve measurement.²⁶ Finally, we attempt to place the analysis of our intriguing data on a more quantitative footing by estimating some quantities of interest using contact mechanics with appropriate simplifying assumptions.

Experimental Section

Sample Materials and Preparation. Poly(ethylene propylene) (PEP) with a weight average molecular weight of 244 000 g/mol and a polydispersity index of 1.7 was used as the matrix for the model adhesive blends. The PEP was obtained by the diimide hydrogenation of polyisoprene³¹ that was synthesized by anionic polymerization. An *n*-butyl ester of abietic acid (nBEAA) was chosen as a model tackifier because its chemical structure is well-known,³² it could be readily synthesized, and it belongs to a 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 50 and 70 μm . Samples denoted as PEP/60 contained 60 wt % tackifier. Both the PEP and PEP/60 samples had homogeneous surfaces.¹⁸

X-Modulation. X-modulation experiments were performed with an Autoprobe CP scanning probe microscope operating in lateral force microscopy mode using the signal access module. The sample was modulated laterally using the built-in piezotube, and the driving voltage and frequency were controlled using a lock-in amplifier (Stanford Research Systems, SR830 DSP) or a commercial D/A converter card installed in the computer. To enhance the precision of the X-modulation experiment, LabVIEW was used to modulate the input voltage, so that the lateral force as a function of forcing amplitude could be collected within 1 min, which is fast enough to minimize hysteresis effects.¹⁸ The displacement of the sample was only a few nanometers, and this amplitude was calculated after calibrating the relationship between applied voltage and piezomovement. All measurements for X-modulation were done inside a glovebox under controlled humidity. 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. The temperature of the water bath and the N_2 flow rate were controlled to adjust the target humidity. A period of 30 min was allowed for equilibration at each humidity.

A schematic of the apparatus used for the X-modulation measurements combined with force–distance curves is shown in Figure 1. The sample was modulated laterally at a frequency of 200 Hz with an amplitude of 2–20 nm at a linear velocity of 800–8000 nm/s using the built-in piezotube controlled by the lock-in amplifier. Simultaneously, the sample was moved vertically toward and then away from the tip at a rate of 10–300 nm/s. 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 signals 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

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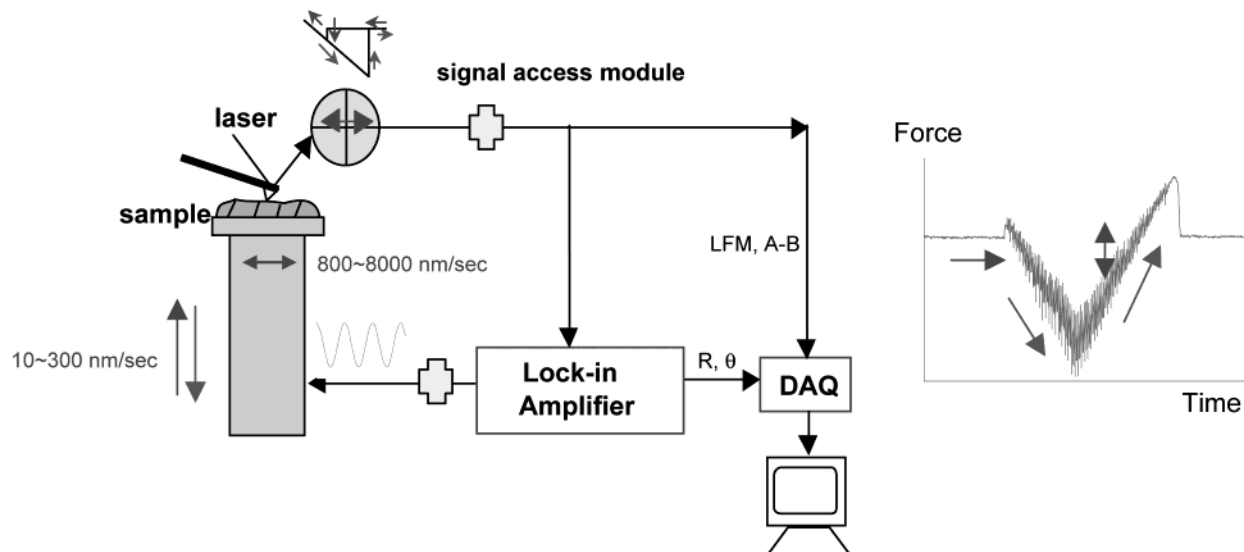


Figure 1. Schematic of the instrumentation used for characterization of the surface by X-modulation with simultaneous collection of a force–distance curve. To the right is shown also the variation of the LFM signal as a function of time for this type of measurement.

the lock-in amplifier and then the processed signals were fed to the data acquisition software.

Results and Discussion

Humidity Effect on Adhesive Surfaces Using X-Modulation. Details of the X-modulation technique have been given elsewhere.^{22–29} 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 half the peak-to-peak amplitude. Previous work has shown¹⁸ that some hysteresis exists in the measurement, which can affect the precision of the data. The extent of hysteresis is related not only to the strength of the surface stickiness but also to the total measurement time. When the feedback was turned off, this hysteresis was markedly reduced. However, some hysteresis was still present, which can result in sample damage and increased measurement uncertainties. To minimize this effect, we collected an entire data set within 30–40 s, a rate 4–5 times faster than that used earlier by us¹⁸ for X-modulation. The faster data acquisition was made possible using computer-assisted measurement automation. A high-speed commercial D/A (digital to analog) conversion card was installed in the computer, and it was controlled by way of the commercial software package LabVIEW.

Figure 2a presents the peak-to-peak amplitude of the oscillating LFM signal from the PEP sample obtained at four different humidities while increasing the forcing amplitude with the z -feedback turned off. Five different positions were examined, and only stick behavior was seen. Even though the magnitude of the measurement uncertainty gradually increases with increasing forcing amplitude, as shown in Figure 2b, when considering the data for the extreme values of relative humidity, one recognizes that there is a slight decrease in lateral force on the PEP surface with increasing humidity. The surface of the PEP/60 sample exhibited behavior sharply different from that of the PEP surface, as shown in Figure 3. At the lower humidity, a maximum in the curve marks a transition

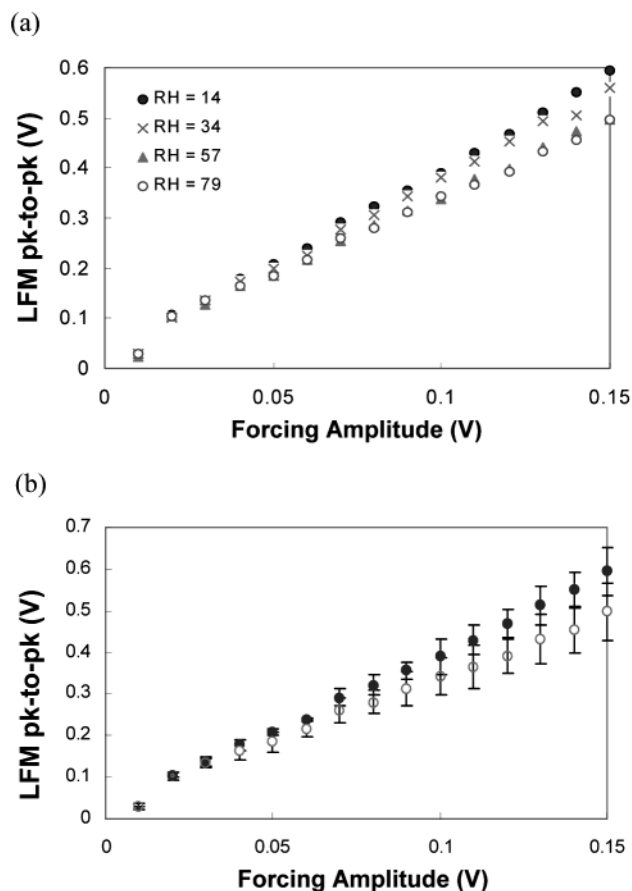


Figure 2. Effect of humidity on lateral force at a PEP surface using normal X-modulation at 200 Hz: (a) average value ($n = 5$) of peak-to-peak lateral force at four different humidities as indicated in the legend; (b) data at the lowest (RH = 14%) and highest (RH = 79%) humidity shown with uncertainties corresponding to one standard deviation.

from stick to slip behavior with increasing forcing amplitude. At higher humidity, stick behavior was seen, on average, over the entire range of forcing amplitude, and the lateral force was enhanced relative to that at low humidity.

The results presented in Figures 2 and 3 differ in some ways from those for other sorts of surfaces reported already

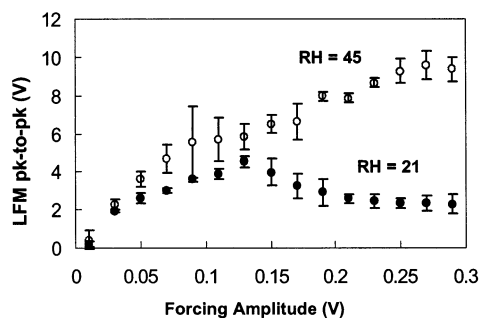


Figure 3. Variation of lateral force with forcing amplitude on the PEP/60 surface measured using normal X-modulation at 200 Hz and two relative humidities: 45% (○) and 21% (●).

by others. In discussing our results, it is helpful to consider if the arguments developed by others are appropriate to our system. It has been reported that, for hydrophilic surfaces such as mica,² silicon oxide,³ and an MoS₂ single layer on mica,⁴ the friction or the friction coefficient decreases with increasing RH at high humidity (over 60–70% RH). The rationale given for this behavior has been that water serves as a boundary lubricant in the contact region in these cases. This trend becomes less important for hydrophobic surfaces, apparently because the water molecules are unable to penetrate the contact junction. A different behavior is observed for hydrophilic surfaces⁴ at low humidity. At low humidity, either no special effect is observed³ or the friction coefficient increases with increasing RH.⁴ The authors⁴ of the study in which this behavior has been reported argue that the behavior is related to the presence of an increased capillary force at higher RH. The increased attraction of the tip for the surface would increase the force necessary to move the surface relative to the tip, that is, the shear force. Even if the details of the explanations vary slightly among papers, most of the arguments share a common characteristic. They are based mainly on the discussion of changes in capillary force with humidity. In general, there is a discontinuous change in the capillary force at low relative humidity between 20 and 40%, depending on the nature of the solid surface. Beyond the transition point, there is not much agreement on the trend. Salmeron and co-workers⁹ and Overney and co-workers⁸ have observed the capillary force decreasing above the transition point (~40% RH). However, their explanations are quite different. While the former group argues this behavior is due to a simple effect of tip geometry, the latter group proposes a mechanism involving an enhancement of the repulsive force through chemical bonding of the liquid in the gap. This argument is based on earlier results of Mate and co-workers.³ However, in some other studies the capillary force is seen to increase gradually with humidity.^{10,11}

The implication of the above discussion is that the effect of water is much more complex than had been previously suspected, a point discussed well by Piner and Mirkin.¹ Moreover, in the case of soft materials, understanding the effect of humidity becomes more difficult due to the presence of surface roughness and deformation of the surface during contact. For example, the hydrophobic surface of a self-assembled monolayer⁵ shows a complicated variation in friction with humidity. Thus, attempts to describe our observations simply drawing connections between the capillary force and relative humidity will probably not be satisfactory.

Another important question is whether our results obtained using X-modulation are comparable to macroscopic data such as values of a macroscopic sliding friction

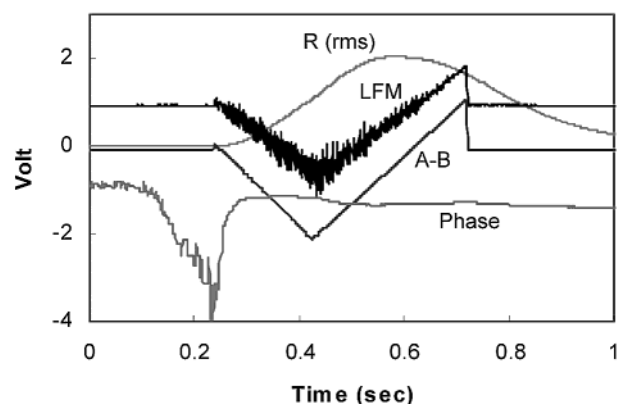


Figure 4. Traces vs time of four signals captured simultaneously during a measurement combining X-modulation with a force–distance measurement with a fast loading rate (360 nm/s). The signal marked “R” is the rms lateral force corresponding to the magnitude of oscillating lateral force (LFM). The “A–B” signal is related to the vertical deflection of the cantilever. “Phase” is the phase difference between the input and output signal. The “LFM” signal is the lateral force signal.

coefficient. Friction measurements on a macroscopic scale are usually used to define the friction coefficient as the ratio of the friction force to normal load, and the friction force is obtained using friction loop scans. As mentioned earlier, surface stickiness itself can be manifested in X-modulation, which is of course the most important parameter for the study of adhesive surfaces. However, surface stickiness becomes much less significant in macroscopic friction measurements due to the role of surface deformation. Under the conditions for macroscopic measurements, the velocity of the tip is sufficiently high to overcome the tendency for the tip to stick to the surface. Both the contact area and the contact time at any point on the surface are reduced relative to an X-modulation measurement.

In any case, it is believed that although the hydrophobic nature of the PEP surface results in no strong interaction with water molecules, a thin water layer could act as a lubricant, which could reduce the frictional force during tip oscillation. The different trend seen for PEP/60 indicates that the interaction between tip and sample increases with relative humidity. We can explain this phenomenon only by assuming that the PEP/60 sample has a tackifier-enriched sticky surface with hydrophilic nature. This hypothesis can be tested using a force–distance measurement ($F-d$) during X-modulation.

Force–Distance Measurement during X-Modulation. One useful extension of the X-modulation technique is its combination with a simultaneous measurement of the force–distance curve, because in this way several pieces of information can be obtained simultaneously. While the adhesive force and apparent stiffness of the surface can be estimated by analyzing the response of the 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 the tip or the viscoelastic properties of the sample. Data acquired during relatively fast loading (360 nm/s) with X-modulation at 200 Hz are shown in Figure 4. Four signals were captured simultaneously over a 1 s period. Vertical deflection of the cantilever (as registered in the A–B signal) is quantified to deduce the normal force on the cantilever, while the rms lateral force, $R = (X^2 + Y^2)^{1/2}$, 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

Table 1. Variation in Properties of PS, PEP, and PEP/60 Surfaces

	experimental conditions			results		
	RH (%)	temp (°C)	forcing amp. (V)	stiffness (nN/nm)	θ_{\max} (deg)	$R_{\text{normalized}}$ (V_{rms})
PS	23	24	0.004	0.30	0.7	0.4
PEP	23	24	0.004	0.073	13.7	0.1
			0.05	0.066	10.3	1.3
			0.1	0.065	9.8	2.5
	77	25	0.004	0.074	13.4	0.1
			0.05	0.066	10.4	1.0
			0.1	0.061	9.9	2.1
PEP/60	23	24	0.004	0.21	0.8	3.2
	40	24	0.004	0.14	1.0	5.7
	77	25	0.004	0.06	3.5	23

uncalibrated lateral force (expressed in volts) is calculated as

$$F = 0.5(\text{peak} - \text{peak}) = \sqrt{2} \cdot \sqrt{X^2 + Y^2}$$

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 the force versus time curve (marked LFM), which is an analogue 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, with 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 marked LFM 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 versus 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 resolution of the detail in the oscillating LFM signal, artifact-free processed signals can be captured by reducing the loading speed to 10 nm/s. An Ultralever B cantilever (normal spring constant = 0.4 N/m) was used in this experiment with a forcing amplitude of 0.004 V, which corresponds to a lateral displacement of the sample of 0.8 nm 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 a glassy polystyrene (PS) film. The third surface was that of poly(ethylene propylene) (PEP). This homopolymer has been 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.^{15,18} 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 ($\theta \sim 20^\circ$) is clear evidence of the slip occurring. When slip occurs, the slope of the loading curve decreases with increasing tip deflection in the force–distance curve³³ and a finite phase lag will be observed, even though the material is elastic.³⁴ Therefore, we used PS as a reference sample for further discussion. Since R is a function of the 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 force–distance experiment using AFM as a tool for nanoindentation. An overview of nanoindentation measurements of polymers has been provided by VanLandingham.³⁵ 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 instrumental uncertainties severely limit their uses as nanoindentors. Despite these limitations, successful studies of polymers have been completed either by reporting the results on a relative basis or by reporting them with large 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 nontrivial process having much higher uncertainty than that for nanoindentation. Therefore, in this contribution, we focus mostly on qualitative and relative comparisons among the different surfaces. However, we have tried to calculate penetration depth and contact radius using appropriate physical parameters and equations, which will be discussed in more detail at the end of this section.

While the response of the PS surface showed behavior typical of glassy materials, such as high stiffness, small R , and small phase lag, the PEP surface clearly showed

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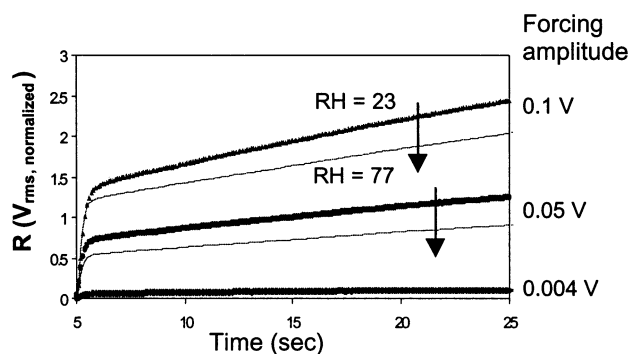


Figure 5. Variation in the X-modulation response with a change in relative humidity from 23 to 77% for the surface of the aged PEP sample when measured using X-modulation in combination with the force–distance measurement. Results are shown for three forcing amplitudes: 0.004, 0.05, and 0.1 V.

different behavior. The small values of stiffness and R_{reduced} and high phase lag for the PEP surface may be related to the liquidlike character of its surface that results in efficient damping of the tip movement. The behavior of PEP/60 was quite different from that seen for the pure polymer. 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 those of 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,¹⁸ we argued that the amplitude of the response to the oscillatory forcing function and the behavior of the “stick–slip” transition are 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 force–distance 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 on the Molecular Interaction of Adhesive Surfaces. The relative humidity of the environment is known to have a strong influence on adhesion,³⁶ 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 the rms response is plotted as a function of time at three forcing amplitudes. $R_{\text{normalized}}$ is given by

$$R_{\text{normalized}} = R_{\text{exp}} / (F_{\text{max,exp}} / F_{\text{max,ref}})$$

$F_{\text{max,ref}}$ is the maximum force from the loading curve in the force–distance measurement for the PEP surface with a forcing amplitude of 0.004 V and 23% relative humidity. 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. This trend is consistent with the result obtained from an X-modulation experiment without the simultaneous force–distance measurement.

The data show that the stiffness of PEP decreases slightly with forcing amplitude at both high and low humidity, even if the order of magnitude is still much smaller than that of PS and PEP/60. It is believed that the normal force is not completely uncoupled from the lateral force, which can result in an extra force being exerted in the direction normal to the surface. This additional force may be increased with increasing sample displacement in the x -direction because R increases gradually with forcing amplitude, indicating that the tip is stuck to the surface under these experimental conditions. At the same time, however, θ decreases gradually with forcing amplitude. Because all measurements were done in the stick regime, this phase change must originate from the viscoelastic nature of the surface and reflect a change in response with shear rate.

The lateral force in response to X-modulation on the PEP/60 surface varied more strongly with humidity than did the response of PEP. Figure 6 shows for the PEP/60 surface the variation of $R_{\text{normalized}}$ and normal force as a function of time for three different relative humidities. The value of $R_{\text{normalized}}$ rises rapidly upon 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 water in the atmosphere and the tackifier. Figure 6b shows traces with time of the normal force, 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 lower at the higher humidity, as evidenced by the lower slope. Also a small curvature appears in the unloading curve. However, when the humidity is increased to 77%, the 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 behavior is observed because the more hydrophilic nature of the PEP/60 surface results in strong, but complicated, interaction with water. Values of quantitative descriptors characterizing the changes with humidity are summarized in Table 1. 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. We believe this behavior is consistent with the presence of a tackifier-enriched surface. It is highly likely that, as a result of the altered 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 will have a lower hardness than does the surface if the surface is enriched in tackifier (especially after aging). It is also possible that the entanglement density of the polymeric blend near the surface may be reduced during this nanoscale contact by water molecules transported to the location by the tip.⁸ Water can act like a plasticizer. Either effect would result in a smaller normal force being observed. Therefore, we conclude that the PSA surface is enriched in tackifier.

This proposed explanation can be further probed by attempting a more rigorous analysis to obtain values of the penetration depth and contact area. In the previous section, we mentioned briefly the limitations and difficulties in obtaining quantitative results from AFM nanoindentation data. Having acknowledged those limitations, we analyze the force–distance data on the basis of Hertzian contact mechanics. The loading

(36) Benedek, I.; Heymans, L. J. *Pressure-Sensitive Adhesives Technology*, 1st ed.; Marcel Dekker: New York, 1997.

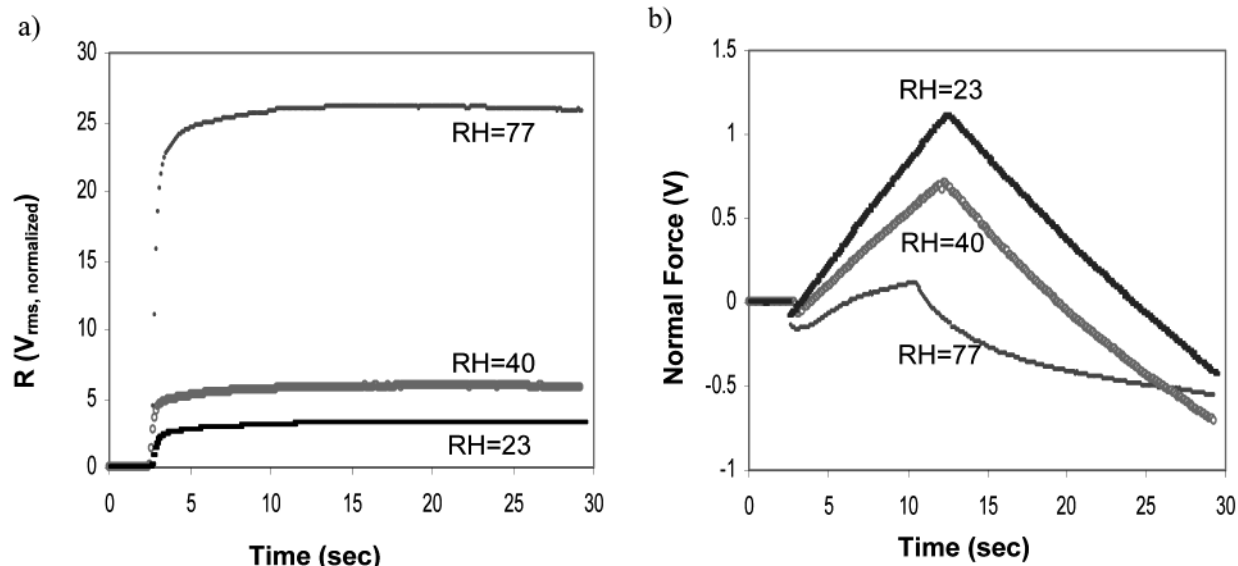


Figure 6. (a) Variation with time in the normalized rms lateral force for the PEP/60 surface at three relative humidities: 23, 40, and 77%. (b) Variation in uncalibrated normal force with time (derived from the A–B signal) for the same experiments for which data are shown in part a.

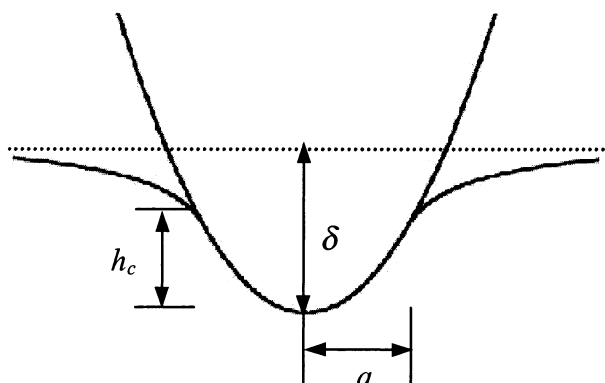


Figure 7. Illustration of the contact geometry.

force can be written as³⁷

$$F = k_{\text{contact}}\delta \quad (1)$$

because Hooke's law connects the deflection of the cantilever and the applied load through the force constant, k_{normal} , of the cantilever, which is related to the total system stiffness, k_{total} , and the contact stiffness, k_{contact} . Here, δ is the penetration depth of the tip. VanLandingham³⁵ recently discussed the analysis of the nanoindentation of polymers using a method of analyzing indentation load–penetration curves based on work by Oliver and Pharr.³⁸ Assuming this approach is applicable to nanoindentation data obtained using SPM, one can calculate the contact depth, h_c , as shown in Figure 7, by

$$h_c = \delta - \frac{\epsilon F_{\text{max}}}{k_{\text{contact}}} \quad (2)$$

where ϵ is a function of the particular tip geometry. Using simple geometrical considerations, the contact radius can be roughly estimated by

$$a = h_c \tan \alpha \quad (3)$$

Table 2. Values of Modulus Estimated Using Herzian Contact Mechanics

	RH (%)	δ (nm)	a (nm)	E_1^a (MPa)	E_2^b (MPa)
PEP	23	143	25	1.8	1.2
PEP/60	23	49	9	26	20
	40	62	11	10	7.8
	77	87	15	2.3	1.8

^a Calculated using eq 4. ^b Calculated using eq 5.

Since we used a conical tip with a half contact angle (α) of 32.5° , ϵ has the value $2(\pi - 2)/\pi$. Therefore, the elastic modulus, E , can be calculated using the following equation^{22,35}

$$E = k_{\text{contact}}/2a \quad (4)$$

The Hertz model also gives a relation between penetration depth and the loading force³⁷

$$F = \frac{2}{\pi} \left(\frac{E}{1 - \nu^2} \right) \delta^2 \tan \alpha \quad (5)$$

Since we used rubber materials, we assumed a value of the Poisson ratio of 0.5. The results of the analysis are summarized in Table 2. Although there are differences in the values of moduli calculated using eqs 4 and 5, the orders of magnitude are the same, which suggests our approach is appropriate.

At normal humidity, the modulus of PEP is calculated to be 1–2 MPa, which seems a reasonable value, though we do not have a measured bulk value to which to compare because this sample has been aged. As mentioned before, analysis of the nanoindentation data obtained by AFM using contact mechanics theory is a nontrivial process. In addition to the critical argument about the validity of applying the contact mechanics to AFM data, there are many uncertainties in the parameter values used. The exact value of the force constant of the cantilever is one important quantity. However, the difference in modulus calculated for PEP and PEP/60 is large enough that we believe relative comparisons are valid, nonetheless. For example, even if we assign an uncertainty of 30% to the value for the normal spring constant of the cantilever, the propagated uncertainty in elastic modulus is only 10–

(37) Domke, J.; Radmacher, M. *Langmuir* **1998**, *14*, 3320.

(38) Oliver, W. C.; Pharr, G. M. *J. Mater. Res.* **1992**, *7*, 1564.

15%, which does not overshadow the order of magnitude difference in calculated modulus between samples.

At high humidity, while the elastic modulus dropped dramatically, R increased by about 10 times. This is quite an interesting finding. Contact radius and penetration depth also increased over 60%, and this effect by itself might increase the lateral force during sample oscillation. However, the changes in contact radius and penetration depth are not large enough to explain such a big change in R . We believe that 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. This idea comes from a comparison with the "rolling ball" method for measuring adhesion. In analyzing results from a "rolling ball" measurement,³⁶ the frictional force is understood to be the sum of two components, the adhesion component, F_{adh} , and the deformation component, F_{def} . The latter is a function of the material properties such as modulus and internal cohesion. However, in the case of PSAs, F_{adh} must be much larger than F_{def} . If the quantity R likewise results from two components, one due to adhesion and one due to deformation, we imagine that such a large enhancement in lateral force is most likely related to an increase in the adhesion component.

The precise way in which the behavior of this nanoscale contact can be related quantitatively to the overall performance of the adhesive must still be explained. We conjecture that the humidity sensitivity seen on the nanoscale may indicate that peel and modulus decrease with increasing humidity because wetting of the adherent by the adhesive is hampered by the presence of a thin layer of water on the surface. Moreover, undesired chemical reaction either within the adhesive or between the adhesive and adherent is possible, and water could act as a plasticizer. In any case, we take the very different

sensitivity to humidity of the PEP and PEP/60 surfaces to be evidence for the presence of tackifier enrichment, and we conclude that mediation of the tip-surface interaction by water molecules is very important in nanoscale contacts where the role of tackifier is significant.

Conclusions

Using the X-modulation technique, one can probe the effect of humidity on adhesion at the surface of a polymer matrix and a model adhesive containing tackifier. While the oscillating lateral force on the surface in the "stick" regime decreases slightly with increasing humidity on the hydrophobic PEP surface, it increases strongly with humidity on the homogeneous surface of the adhesive loaded with 60 wt % tackifier (PEP/60). To better understand how the humid environment affects the nanomechanical properties of the adhesive surface, the X-modulation technique was combined with a force-distance curve measurement. This approach yields a more precise and reproducible characterization. It is concluded that X-modulation is an appropriate method for the study of nanomechanical properties, especially at adhesive surfaces. A large oscillating lateral force (from X-modulation) and small stiffness (from the force-distance measurement) for PEP/60 at high humidity are consistent both with a model that envisions a tackifier-enriched region within 50–100 nm of the surface and with the hypothesis that at a hydrophilic surface water molecules may strongly alter the surface-tip interactions or modify the mechanical properties of the material nearest the surface. Further clarifying the relative importance of these contributions is the subject of current study.

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