

Resolving Lateral Variations in the Frequency Dependence of Adhesive Properties at the Surface of a Model Pressure Sensitive Adhesive

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ABSTRACT: A commercial scanning probe microscope may be used to laterally resolve qualitative differences in the frequency dependence of material properties at the surface of a model pressure sensitive adhesive (PSA). In a heterogeneous PSA made from polyisoprene and a wood rosin derivative, both the polymer-rich matrix and tackifier-rich domains regions at the surface appear stiffer and show higher adhesive force when increasing the testing frequency from 0.01 to 1 Hz at room temperature. The limited frequency range of the instrument and piezo creep constrain the applicability of the approach. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 400–404, 2002; DOI 10.1002/app.10369

Key words: adhesives; atomic force microscope; mechanical properties; surfaces

INTRODUCTION

All PSA applications involve bond formation and debonding steps. To have good performance, it is necessary for PSA materials to simultaneously possess both liquid-like flow behavior upon application at low frequencies and solid-like strength upon debonding at higher frequencies.^{1,2} The surface and near-surface rheology of a PSA plays a key role in these processes, but is difficult to study. Recent research has shown that measurements of adhesive topography and mechanical behavior using the scanning probe microscope (SPM) can be helpful in understanding pressure-sensitive adhesives. In particular, SPM offers a means of distinguishing the presence of lateral segregation at adhesive surfaces and characteriz-

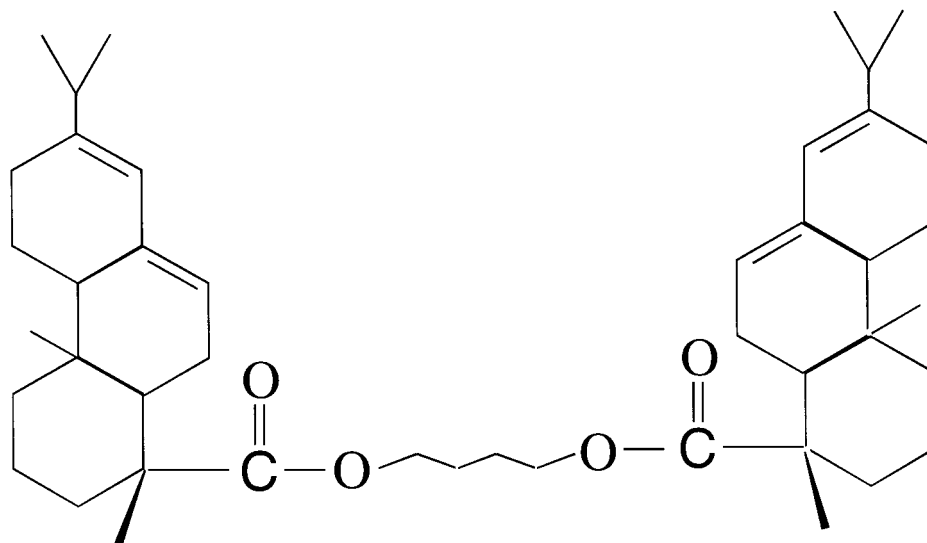
ing the differences in stiffness and local deformation behavior among various regions on the surface.^{3–8} So far, these measurements have not addressed the variation in properties with frequency. However, understanding the frequency dependence of the viscoelastic behavior of pressure-sensitive adhesives (PSAs) is the key to understanding the overall behavior of these materials.

Tsui and coworkers⁹ have looked at the frequency dependence of F-d curves for an adhesive homopolymer, poly(tert-butyl acrylate) using a home-built apparatus. They present plots showing how the shapes of the F-d curves change with both frequency and temperature, and focus on the use of variations in pull-off force with temperature and frequency to identify a glass transition of the sample surface. Force-distance measurements or “nanoindentation” measurements provide a microscopic analog to macroscopic tests of adhesive performance such as the probe tack test. Therefore, F-d measurement at different sweep frequencies should be useful for characterizing the performance of PSAs.

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Scheme 1 Chemical structure of diester abietic acid used in this model pressure-sensitive adhesive.

Here we present measurements of the frequency dependence of force–distance curves collected with a commercial scanning probe microscope from an inhomogeneous blend model of a PSA. As anticipated, the adhesive response is seen to be strongly sensitive to the frequency of measurement over a frequency range of 0.01 to 1.0 Hz. Limitations in obtaining frequency-dependent behavior with a commercial SPM are discussed. These limitations constrain the analysis here to be qualitative in nature.

EXPERIMENTAL

PSAs blends were made with anionically polymerized polyisoprene (PI) and 15, 30, 45, 60, and 80 wt % of a model additive with structure and properties similar to those of commercial tackifiers of the wood rosin derivative family.¹⁰ For the demonstration of the frequency-dependent effects that can be studied with SPM, we focus here on the blend with 15 wt % additive. The number-average molecular weight and polydispersity of the PI were 320,000 and $M_w/M_n < 1.1$, respectively. The T_g of the PI was -62°C . The additive was a diester of abietic acid with a glass transition temperature of about 10°C . Its structure is shown in Scheme 1. Szczecinski¹⁰ performed differential scanning calorimetry scans on samples five days after casting using a TA 2910 DSC and scanning from -100 to 40°C at $10^\circ\text{C}/\text{min}$. Glass

transition temperatures were determined from the first run and verified by the second run. For the sample with 15 wt % only a single transition could be clearly discerned at a temperature (-61°C) only slightly higher than the T_g of the pure PI. However, the transition was considerably broader in the blend, and it has been assumed here that this transition temperature is characteristic of the polymer-rich matrix. Films cast from toluene solution were turbid by visual inspection, indicating that the samples were phase separated, and lateral phase separation was observed at the surface with SPM. The thickness of films was around $50\ \mu\text{m}$.

SPM imaging and force–distance measurements were performed when the samples were two weeks old using an AutoprobeTM CP (Park Scientific Instruments) under ambient conditions and commercial UltraleverTM silicon probes with V-shaped cantilevers. The corresponding force constant was experimentally determined to be about $0.4\ \text{N/m}$ following the procedure of Tortonesi et al.¹¹ The dynamic mechanical properties of PSAs were probed qualitatively by observing changes in the shape of the F-D curve when changing frequency from 0.01 to 1 Hz. To obtain each F-D curve the piezo underneath the sample was first extended $0.04\ \mu\text{m}$ to collect the “loading curve” and then retracted a distance of $2\ \mu\text{m}$ to collect the “unloading curve.” The large retraction distance was necessary due to the tendency for

the sample to adhere tenaciously to the probe tip over a long distance upon retraction.

RESULTS AND DISCUSSION

A topographic image of a typical sample with 15 wt % tackifier is shown in Figure 1. This model blend displayed a two-phase surface morphology containing domains and matrix. From the light tapping, contact, and lateral force mode images of the same area, it was found that the domains were stiffer than the matrix at the frequencies used in these measurements. From other work¹² it is known that this stiffness results from the domains being enriched with tackifier compared to the overall composition of the adhesive. The matrix is rich in polymer. Neither the composition of the matrix nor the composition of the domains is known precisely. Because the samples were stored in air, both the PI and tackifier aged somewhat with time due to oxidation and crosslinking. Thus, the miscibility changed with time. Previous studies of other model PSA blends have tracked changes of this sort with time at ambient conditions.^{13,14}

Figures 2 and 3 show the F-D curves obtained at sweep frequencies of 1, 0.5, 0.1, and 0.01 Hz from the PI-enriched matrix and tackifier-enriched domains, respectively, of a sample with 15 wt % diester. The overall shape of the F-D curve varies with frequency. Loading curves for the tackifier-rich domains are all essentially vertical,

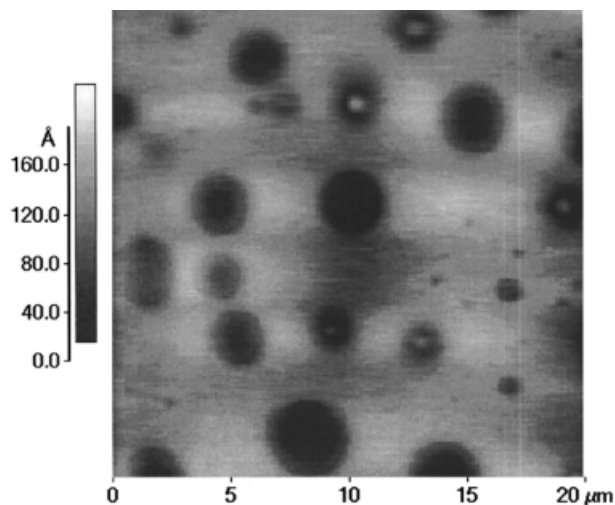


Figure 1 Topographic image of the model PSA films with 15 wt % tackifier measured after 2 weeks in air. Measured using light tapping.

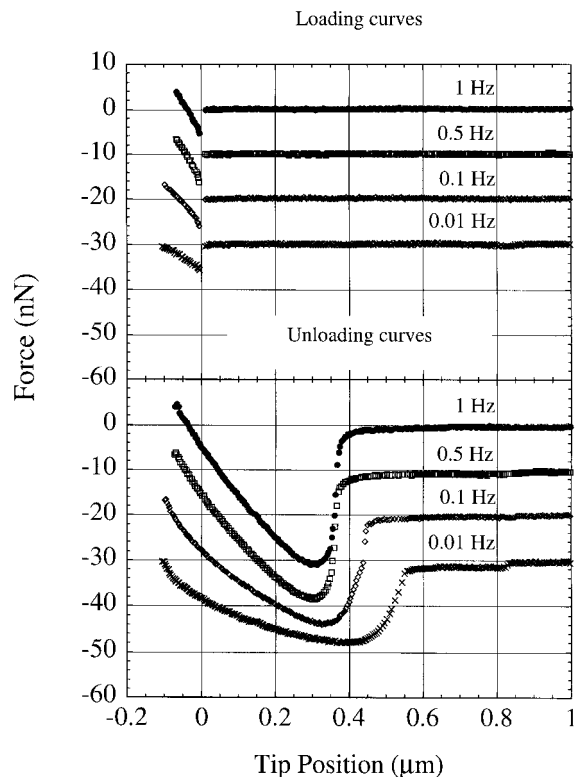


Figure 2 Force vs. distance curves taken over the frequency range of 0.01 to 1 Hz for the PI-enriched matrix of the sample with 15 wt % tackifier.

indicating that the contact stiffness of the domains exceeds that of the cantilever at all frequencies considered. The maximum penetration depths change markedly for reasons explained below. For three frequencies the unloading curves are essentially straight, with a slope dictated by the stiffness of the cantilever.

Only at the lowest frequency is changing of the slope characteristic of relaxation of the domain seen. In each case pull-off is abrupt, with the maximum pull-off force observed at the highest frequency.

For the PI-rich matrix, the unloading curve exhibits continuous deformation over a large retraction distance in each case. As frequency is increased the surface behaves as though it were stiffer.⁹ The slopes of the linear portions of the loading curves and the slopes of the initial portions of the unloading curves both increase. The slope of the initial portion of the loading curve is the best indicator of stiffness upon retraction because there the contact area is thought to change least rapidly. Steeper slopes correspond to higher apparent moduli, although to obtain quantitative

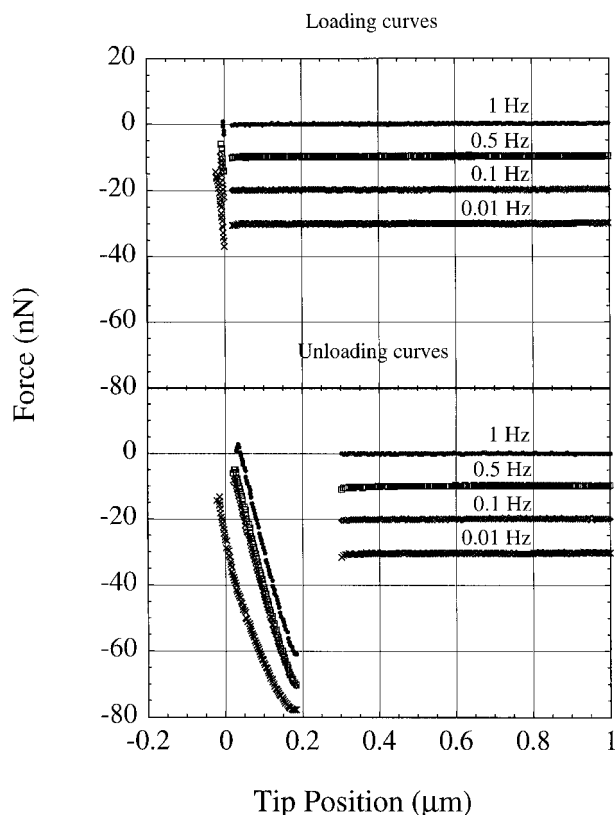


Figure 3 Force vs. distance curves taken over the frequency range of 0.01 to 1 Hz for the tackifier-enriched domains of the sample with 15 wt % tackifier.

comparisons^{15,16} one must account for the precise value of contact area, and no attempt has been made here to estimate that important quantity.

As frequency increases, the retraction portion of the F-D curve observed for the matrix also looks more and more like those measured from the domains. The distance of retraction required for the tip to separate from the adhesive decreases. Release is more abrupt. With increasing sweep frequency, the maximum adhesion force also increases. In this blend the tackifier rich domains are glassy at this temperature for all of these frequencies, so the frequency dependence of the PI enriched matrix dictates changes in the overall surface performance with frequency.

The maximum penetration depth decreases and maximum stress upon loading increases with increasing frequency. The maximum penetration in the PI enriched matrix does not correspond to a maximum stress at 0.01 Hz. In that case, the real contact time is about 2 s and the real stress at maximum penetration is about zero. Arendt et al.¹⁷ indicate the characteristic relaxation time of

bulk PI (M_w , 300 K) (taken as the time in which the response to a step change drops to 1/e times the initial response) is about 7 s at 22°C. So at this frequency of 1 Hz the matrix is modestly plasticized by a small composition of the diester.¹⁷ One would like to probe the range of behavior all the way from this slow extreme to the high rate extreme in which the matrix appears glassy. However, the commercial SPM used here cannot cover the large rate range corresponding to the transition from a glassy state to flow while measuring at only one temperature. In the near future we will expand the frequency dependence study by changing temperature as well.

Another limitation in performing these measurements is caused by creep of the piezo scanner. When the piezo is required to travel over longer distances, the final position of the piezo upon loading just before retraction depends on the rate of movement. Even though the same travel is specified, for slow movement the piezo travels slightly farther. These small differences manifest themselves in the maximum depths and stresses reached in the loading curves. To assess the magnitude of the effect, F-D curves (not shown) were measured on mica using the same travel and frequencies used here. When running at 0.01 Hz the maximum force seen upon loading the hard surface is about 15 nN. For a loading rate of 1 Hz this value drops to about 2 nN. Reducing the travel of the piezo eliminates this artifact, but with the portions of the PSA surface that deform markedly on retraction, reducing the travel is not possible. This limits the applicability of studies with varying frequency to qualitative comparisons.

CONCLUSION

The frequency dependence of the stiffness and adhesiveness of material at the surface of a model PSA can readily be studied qualitatively in different regions on the surface using a commercial scanning probe microscope and its standard software. For the heterogeneous model blend studied here, variations in the polymer-rich matrix were predominant in determining variations in the overall surface response in the frequency range available for testing at room temperature. The behavior of the tackifier-rich domains changed very little when varying the test frequency from 0.01 to 1 Hz. At 0.01 Hz no appreciable stress is generated upon loading, indicating that the char-

acteristic frequency of polymer segment relaxation in this case is higher than the test frequency.

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