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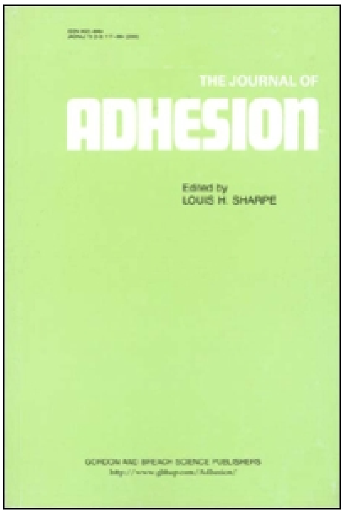

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Paiva, Adriana and Foster, Mark D.(2001) 'Aging of Model Pressure Sensitive Adhesives Studied with Scanning Probe Microscopy', The Journal of Adhesion, 75: 2, 145 — 160
To link to this Article: DOI: 10.1080/00218460108029598
URL: http://dx.doi.org/10.1080/00218460108029598

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J. Adhesion, 2001, Vol. 75, pp. 145–160
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Aging of Model Pressure Sensitive Adhesives Studied with Scanning Probe Microscopy

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(Received 27 July 1999; In final form 30 June 2000)

Changes in the surface morphology and surface friction of a tackified model pressure sensitive adhesive (PSA) with aging have been observed directly with atomic force microscopy. Changes over many months at room temperature as well as changes during brief exposure to two elevated temperatures (65 and 100°C) were characterized. Performance of the PSA, consisting of poly(ethylene propylene) with *n*-butyl ester of abietic acid as the tackifier, was studied qualitatively with nanoindentation.

Tackifier-enriched domains at the blends' surfaces grew and then coalesced with aging and the surface friction decreased as a result. Also, the polymer-enriched matrix stiffened with time. These two effects led to a stiffer surface, poorly suited to wetting an adherend. Domain coalescence was markedly accelerated upon brief exposure to a temperature ramp up to 100°C. At the highest temperatures studied, degradation of the polymeric matrix decreased its stiffness.

Keywords: PSA; Tackifier; Aging; AFM; LFM

INTRODUCTION

To exploit fully the possibilities afforded by adhesives, it is imperative to quantify how adhesive structure and performance change with age and ultimately to develop systems resistant to aging. Conventional techniques used to measure these properties characterize the *bulk*

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behavior of the adhesive as distinct from *surface* properties that are probed in this study.

In the past few years a great deal of attention has been paid to the study of the structure and properties of surfaces due to their importance for practical applications. Since the development of the Atomic Force Microscope (AFM) [1] new areas of inquiry have evolved. The numerous variants of scanning probe microscopy (SPM) available today allow the study of the surface structure and properties of polymeric samples in general and adhesives in particular. Gilicinski and coworkers [2] have used AFM to study the effect of latex coalescence on adhesion performance. Bistac *et al.* [3] showed that there are correlations between the surface deformation observed by AFM and the peel energy. In a similar study, Ryschenkow *et al.* [4] examined failure surfaces in the stick-slip regime and proposed a mechanism of failure for this regime. Studies done previously in our research group [5] have probed the local adhesive properties of model PSAs not only by imaging the sample and obtaining information on the surface morphology, but also by using the tip of an AFM as the probe of mechanical properties. In this paper, the use of AFM to study changes in surface morphology and friction with aging of a model PSA is presented and the implications of these changes for adhesive performance considered.

EXPERIMENTAL

Sample Materials and Preparation

Poly(ethylene propylene) (PEP) obtained by diimide hydrogenation of high *cis* 1,4 polyisoprene was used as the rubbery component of the model PSAs. The PEP had a weight average molecular weight of 244,000 g/mole and a polydispersity index of 1.7. The model tackifier was *n*-butyl ester of abietic acid (*n*-BEAA), a monoester of a rosin acid with T_g of $-45°\text{C}$. By way of comparison, we note that commercial tackifiers of the rosin ester family are blends of triesters and tetraesters having higher molecular weights and glass transition temperatures. It is in this sense of having well-defined composition and molecular structure for both the tackifier and polymer that the PSA used here is a "model". The *n*BEAA tackifier decreases the low-frequency modulus to meet the Dahlquist criterion and also increases the adhesive's glass transition temperature slightly, but the PSA's overall performance is quite modest by commercial standards.

PEP/*n*-BEAA blends were made for several compositions in the range of 10 to 80 wt.% tackifier. (The composition of a blend will be denoted as PEP/*x*, where *x* is the weight percent tackifier loading.) All samples were prepared by solution casting on microscope slides from solutions in toluene using an Accu Gate^{TM} fluid spreader. Film thicknesses ranged between 50 and 75 µm.

The model adhesives showed a two-phase morphology at room temperature, as observed by optical microscopy, at compositions above 15-wt.% tackifier [6]. Examination of the surface morphology by AFM revealed that all but one blend had heterogeneous surface morphologies as well. The PEP/60 blend had a homogeneous layer at the surface [5]. AFM also revealed that the sample of PEP/10 was phase separated, having very small domains (less than one µm in size) not resolvable by optical microscopy.

Aging of the Adhesive Films – Time and Temperature

Aging of two types was considered: aging at room temperature over many months and also aging during brief exposure to a rapidly rising temperature. In one series of measurements samples were stored at room temperature and humidity in the dark (*e.g.*, stored in a closed box inside a drawer). The samples were examined three and a half months, seven months, ten months, one year, and nineteen months after being cast.

The effects of brief temperature excursions on the surface morphology and friction properties were also studied by annealing the samples at 65°C and 100°C, after they had been stored at room temperature for about a year. The temperature was ramped up at a constant speed of 1°C/min to the annealing temperature on a hot stage, the sample left for one minute at the annealing temperature, and then cooled to room temperature. Imaging of the sample surface was then done in contact mode.

SPM Measurements: Atomic Force Microscopy (AFM) and Lateral Force Microscopy (LFM)

Scanning Probe Microscopy measurements were performed as described recently [5] using an Autoprobe$^{\text{TM}}$ M5 from Park Scientific Instruments. Silicon probes (Ultralever$^{\text{TM}}$, Park Scientific Instruments) with V-shaped cantilevers and conical tips with typical radius of curvature $\sim 10\,\text{nm}$ were used for all measurements. The spring constant of the cantilevers was experimentally determined to be $0.41 \pm 0.03\,\text{N/m}$ following the procedure described by Tortonese *et al.* [7]. Topographic (AFM) and friction (LFM) images of the surfaces of the samples were obtained under ambient conditions in contact mode according to established procedures [8–10]. Under these conditions a thin layer of adventitious material coats the surface and influences the interactions between the tip and the surface. Nonetheless, the relative behavior of samples studied under the same conditions can be compared.

Nanoindentation

Local mechanical properties at the surface were studied by nanoindentation where the tip of the AFM was used as the probe. Force–displacement ($F-\delta$) curves were acquired along a line to determine differences in properties between the domains and matrix and to monitor changes, if any, with aging time and temperature. At present, only relative values can be obtained from $F-\delta$ curves obtained by AFM since the contact area, tip/sample interactions and geometry of the tip have to be precisely known to give absolute values of the adhesive forces and energies [5, 11]. $F-\delta$ measurements probe the mechanical properties of about the first 150 nm of material next to the surface.

RESULTS AND DISCUSSION

Aging at Room Temperature

All the samples except PEP/60 showed an increase in the sizes of domains with time and for times greater than 10 months the domains started to coalesce. The PEP/60 blend appeared to form a homogeneous layer at the surface [5] and showed no change in the surface structure with time.

Topographic images of PEP/10 are shown in Figure 1. Only a slight increase in the sizes of the domains was observed at 7 months, but after 10 months coalescence of the domains was observed. At nineteen months the domains had grown considerably. The fraction of the surface covered by "matrix" material decreased with time. Nanoindentation measurements, LFM measurements, and the preferential dissolution of the domains by acetone all indicated that the domains seen in the blends with 10 and 80 wt.% tackifier were tackifier enriched [5]. Results for a blend with 45 wt.% tackifier are shown in Figure 2. This sample presented two kinds of domains that appear dark and

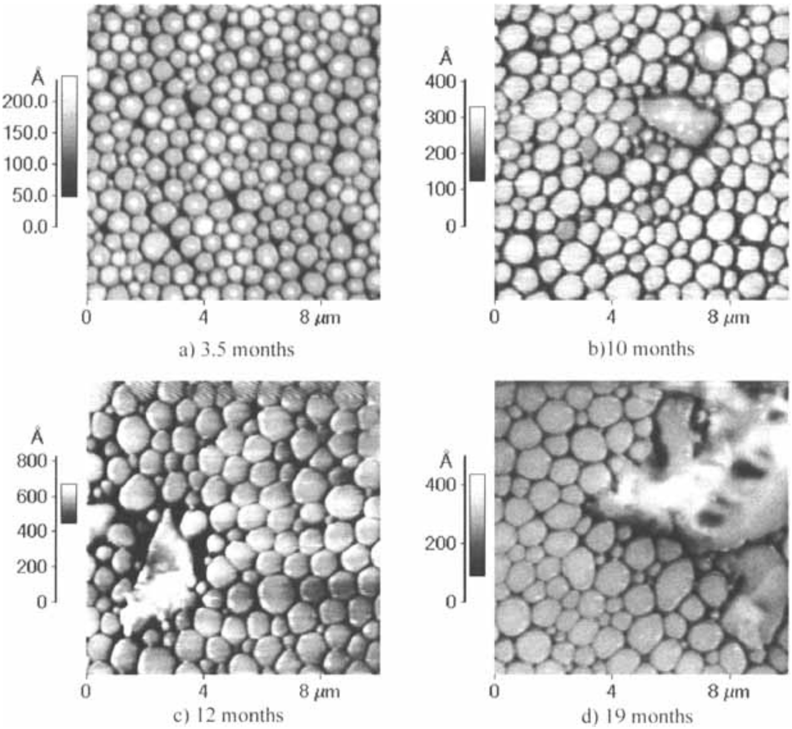


FIGURE 1 Topographic images of PEP/10 after four different times of annealing at room temperature. The domains gradually grow with aging and coalesce. (See Color Plate I).

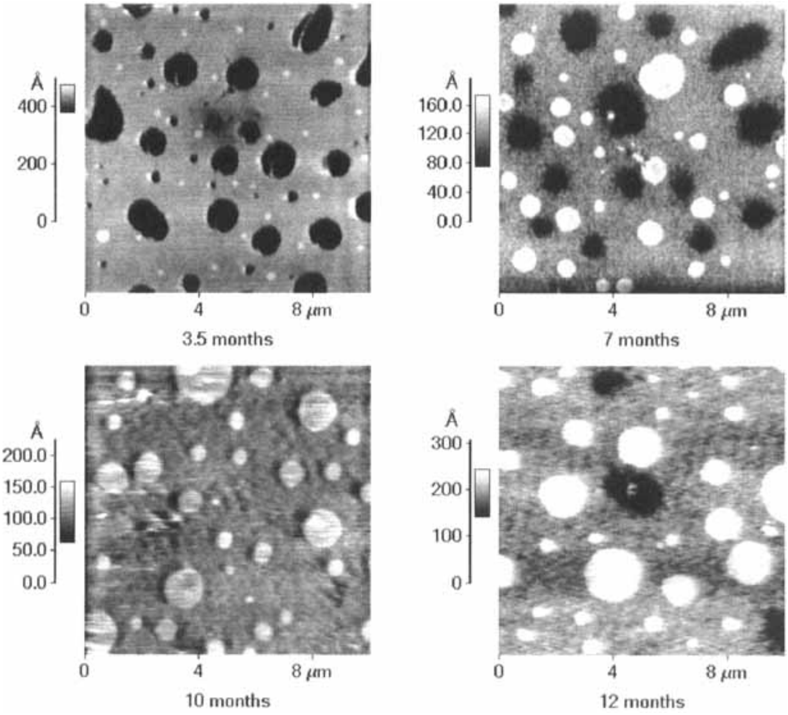


FIGURE 2 Topographic images of PEP/45 after four different times of annealing at room temperature. The domains richest in tackifier appear bright. These become larger and more numerous with aging. (See Color Plate II).

light in the images. The darker domains exhibited $F-\delta$ curves more similar to those of the pure PEP, indicating that the darker domains had a lower composition of tackifier than did the domains that appear light in the images. The domains more strongly enriched in tackifier were stiffer and behaved like the tackifier-enriched domains seen at other blend compositions. The matrix showed a behavior intermediate between that of the two types of domains. At a composition of 45 wt.% both the size and number of the polymer-enriched domains (dark areas) decreased with time. Concurrently, the tackifier-enriched domains increased in size and number. Increasing enrichment of the surface in tackifier would be expected to make the surface increasingly rigid, hindering the ability of the adhesive to wet a surface and degrading the adhesive performance.

The gradual change of the surface composition with time indicated indirectly by these results suggests that the kinetics of the aging process are not dictated simply by migration of the tackifier. In separate experiments [12] we have measured the mobility of this tackifier in PEP blends and confirmed the expectation that the tackifier moves quite rapidly. That is, the self-diffusion coefficient is about $8 \times 10^{-9}\,\mathrm{cm}^2/\mathrm{s}$ for a composition of 45 wt.% *n*-BEAA. While the mutual diffusion is controlled by the thermodynamics of the blend, further study [6] also indicated that these blends are not in states close to the system spinodal and, therefore, there should not be appreciable "thermodynamic slowing down" [13, 14] in this system. Thus, the components of the system, at least at the surface, must themselves be changing, causing a shift in the thermodynamic balance at the surface. Unstabilized abietic acid derivatives are thought to degrade by the formation of small amounts of hydroperoxides [15] over periods of days at room temperature. These hydroperoxides are stable at ambient temperature, but upon heating may decompose and induce further degradation. The polymer can also change somewhat with time (see below). Thus, the components in the system after a few months are not the same as those present initially.

Nanoindentation experiments were performed to gain information on the local adhesive character of the films. When a nanoindentation experiment starts, the cantilever is above the surface. The cantilever does not deflect and zero force is recorded. As the tip is brought closer to the surface, it jumps into contact at point "a" in Figure 3 (snap-in force). Once in contact with the sample, the cantilever's deflection will increase as the sample and cantilever are closer to each other. If the cantilever is sufficiently stiff, the probe tip may indent the surface. In this case, the slope of the part of the curve corresponding to contact can provide information about the stiffness of the sample. After loading the cantilever to a desired force (point "b") the process is reversed, passing through the point of minimal force (point "c"). The difference between this minimal force and the zero force is defined as the snap-out force or adhesive force. The area between the loading and unloading curves gives the total dissipated energy or adhesive energy.

Nanoindentation results for pure PEP, shown in Figure 3a, indicated that it became stiffer with time, probably due to crosslinking. This polymer was prepared by the diimide hydrogenation of

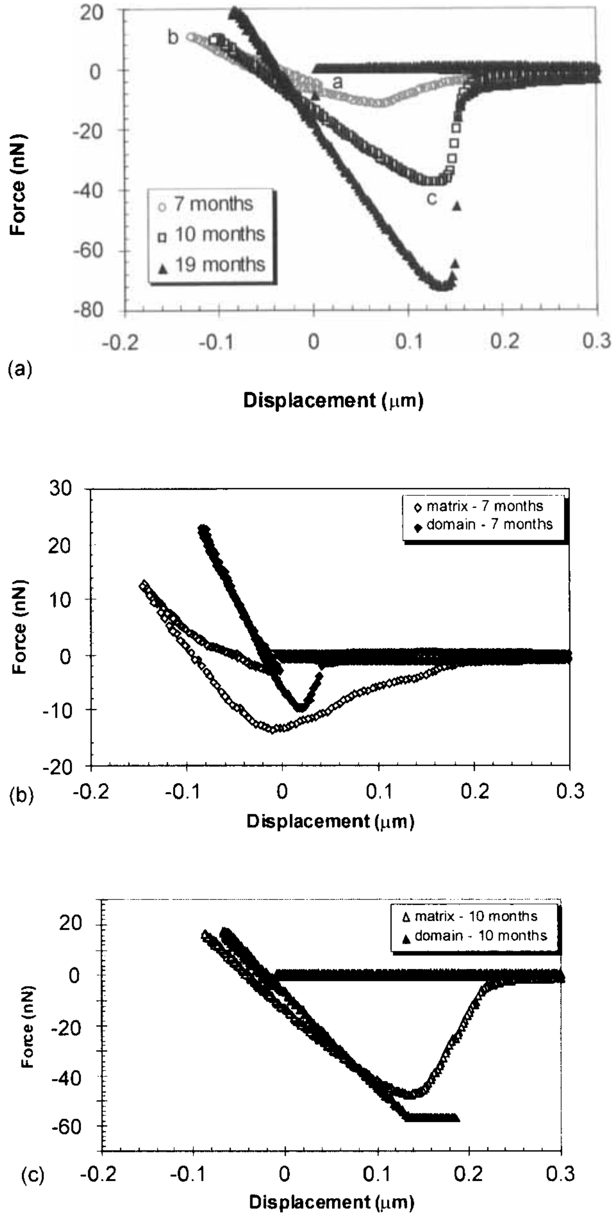


FIGURE 3 Force-displacement curves after aging at room temperature and humidity: (a) for PEP at 7 months, 10 months and 19 months, (b) PEP/10 at 7 months, (c) PEP/10 at 10 months, (d) PEP/10 at 19 months. In all curves some data points have been removed to improve clarity.

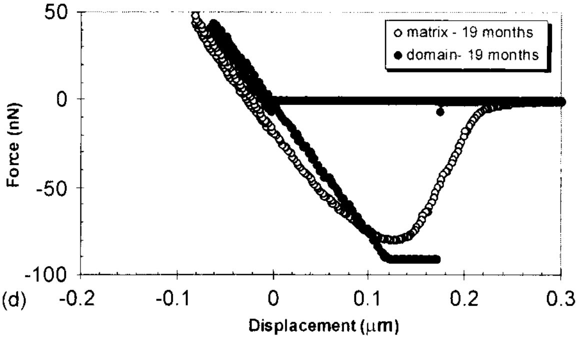


FIGURE 3 (Continued).

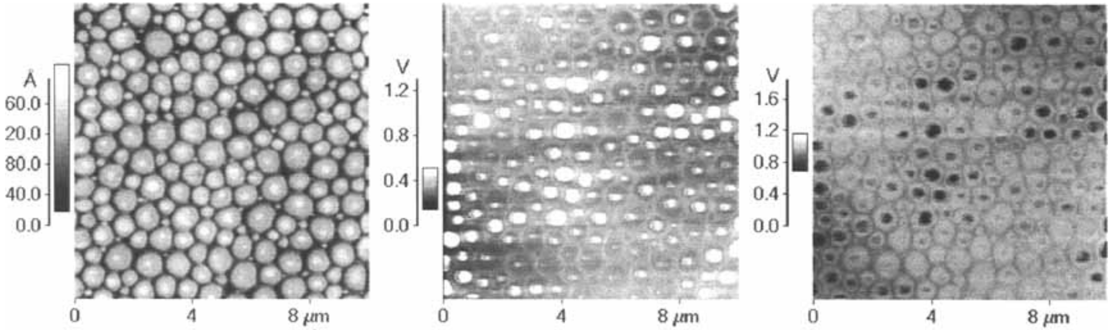
polyisoprene. In this reaction, contaminants were introduced in the polymeric chains from the reaction of *p*-toluenesulfonic acid (a byproduct of the hydrogenation process) with vinyl groups present in the polymer, yielding sulfones and sulfides that can lead to crosslinking and stiffening of the polymer [16, 17]. Molecular weight determination was done by size exclusion chromatography (SEC) for the film of pure PEP that had been aging for 19 months. The weight average molecular weight of the soluble fraction had increased about 16%. The presence of non-soluble material was also observed. These two results indicate polymer crosslinking.

The variation of force–displacement ($F-\delta$) curves with time was examined for three blends: PEP/10, PEP/60 and PEP/80. It was observed that for the two blends that showed two-phase morphologies at the surface (PEP/10 and PEP/80) both phases became stiffer with time. The change in the $F-\delta$ curves was most pronounced for the matrix phase. Since the matrix was polymer-enriched [5] it was expected that the biggest changes would occur in the matrix. Figures 3b–d show the force–displacement curves for the blend of PEP/10 at three stages of aging. After seven months aging there was a striking difference between the $F-\delta$ curves in the domains and matrix, but with further aging the $F-\delta$ curves of the tackifier-enriched domains and of the polymer-enriched matrix became more similar to each other. This behavior indicated that the effect of stiffening of the polymer influenced the overall behavior of the PSA on a nanoscale level. The curves obtained for 10 and 19 months in the domains showed signal saturation (no change in force with displacement) just prior to pull off, as shown in Figure 3b. This indicated that the cantilever was not sufficiently stiff to measure the total adhesive energy quantitatively.

Aging at Elevated Temperature

In order to study directly what would happen with more severe aging, one set of samples at all compositions was exposed to elevated temperatures after it had already aged for about one year at room temperature. All the samples were warmed up to 65°C as described above. Topographic and friction images taken after this treatment for the sample with 10-wt.% tackifier are shown in Figure 4. There was no noticeable increase in the sizes of domains in any of the samples after this treatment. Three samples with tackifier compositions of 10, 60 and 80 wt.% were selected to be further annealed at 100°C. The samples with 10 wt.% tackifier showed marked increases in the sizes of the domains after exposure to this temperature, as demonstrated in Figure 4. The effect was less strong for the sample with 80 wt.% tackifier as shown in Figure 5. However, the sample of PEP/60 showed no change and its surface remained homogeneous. Therefore, the sample with 60 wt.% tackifier was then heated up at 1°C/min to an even higher temperature of 150°C. The film became yellow due to degradation, probably primarily of the polymer, but no changes in morphology of the surface were observed by AFM.

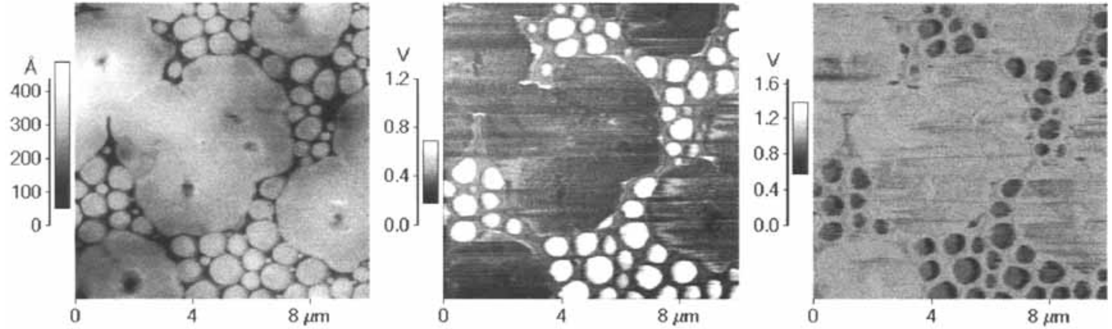
Further information regarding the changes that took place upon annealing was obtained from the images of the friction of the surface. For the case of PEP/10, the small domains appeared as bright regions in the LFM images while the coalescent domains appeared as darker regions (left-to-right image). The opposite contrast was observed in the right-to-left images. These results indicated that there were differences in friction among the domains, the matrix and the coalesced domains. When the domains coalesced they exhibited lower friction than when they were still small. This suggested an aging mechanism for these model PSAs. The reduction in friction could be explained as follows. When the temperature was increased to 100°C, the surface enrichment of tackifier was more pronounced, creating a stiffer surface and reducing the friction. This decrease in friction also indicated that in



a) Topography. T=65 °C

b) LFM, left-to-right. T=65 °C

c) LFM, right-to-left. T=65 °C



d) Topography. T=100°C

e) LFM, left-to-right. T=100 °C

f) LFM, right-to-left. T=100 °C

FIGURE 4 Change in topography (a) and (d) and friction (b), (c), (e) and (f) with exposure to 65°C (top images) and 100°C (lower images) for PEP/10. (See Color Plate III).

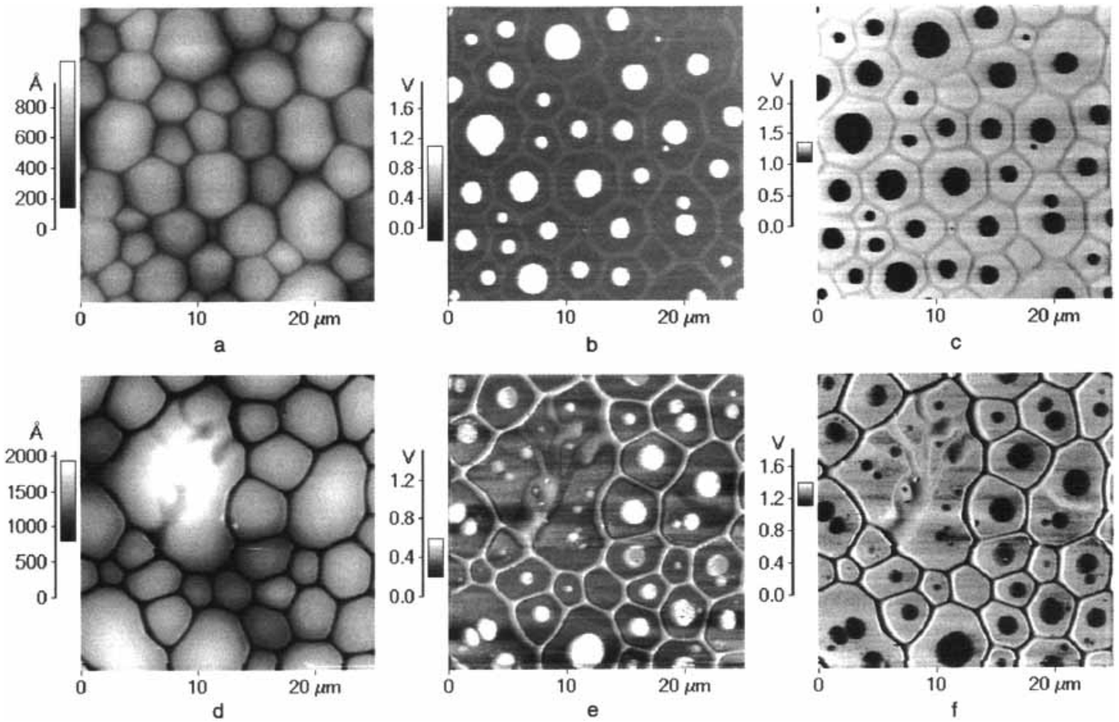


FIGURE 5 Changes in topography (a) and (d) and friction (b), (c), (e) and (f), with exposure to 65°C (top images) and 100°C (lower images) for PEP/80. (See Color Plate IV).

these areas the surface was less sticky than before annealing the sample at 100°C.

The PEP/80 sample behaved similarly. Before the temperature treatment (not shown) and after increasing the temperature to 65°C the tackifier-enriched domains showed areas within the domains that had higher surface friction, as shown in Figure 5. A pronounced increase in the domains sizes was observed after heating the sample to 100°C. In the coalesced domains the bright areas with higher friction were significantly reduced. Only very small bright areas were observed in the biggest coalesced domain. Friction in the domains was decreased, indicating that these areas were less sticky. LFM images of PEP/60 showed no change in friction with the temperature excursions, even after exposure at 150°C.

Force–displacement curves acquired by nanoindentation measurements with the tip of the AFM before and after annealing for PEP/10 are shown in Figure 6. For the curves acquired in the tackifier-enriched domains (Fig. 6a) an interesting behavior was observed at 100°C. The value of adhesive force was smaller for the coalesced domains than for the small domains which had not coalesced. The snap out was also more abrupt. This result correlated well with the LFM results since the coalesced domains showed lower friction than did the small domains. The slope of the loading part, which is proportional to the modulus of the sample, did not change with annealing temperature. This result

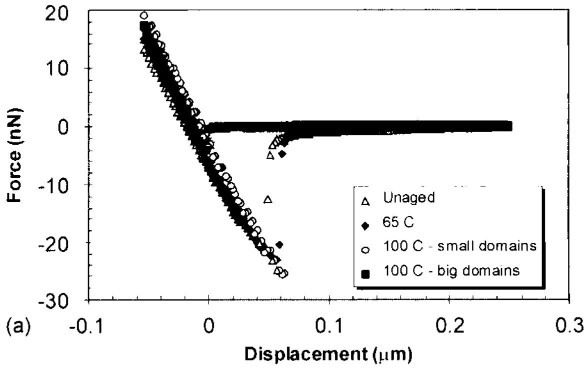


FIGURE 6 Force–displacement curves measured for the PEP/10 blend at different points of aging with temperature, (a) in the domains; (b) in the matrix. In all curves some points have been removed to improve clarity.

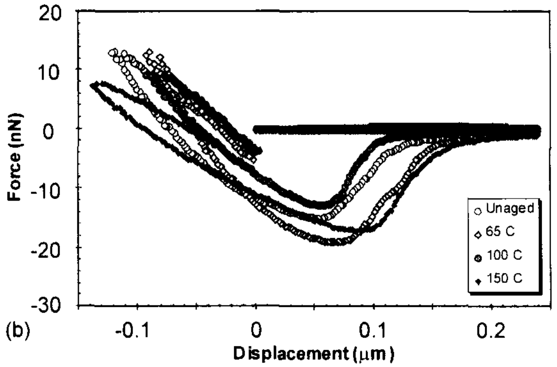


FIGURE 6 (Continued).

highlighted the fact that SPM techniques compliment one another. LFM probed variations in the friction properties at the surface while nanoindentation measurements probed into the "bulk" of the sample at very small penetration depths. These results indicated that changes in friction due to surface enrichment of tackifier were only a surface effect. The stiffness, even at very small penetrations probed by nanoindenting the sample, remained unchanged. This behavior was observed as well for PEP/80. The blend of PEP/60, which had a tackifier-enriched homogeneous layer at the surface, did not show any changes in the $F-\delta$ curves even after exposure to a temperature of 150°C.

Nanoindentation results for PEP/10 in the polymer-enriched matrix are shown in Figure 6b. After exposure in air to a temperature of 65°C there was a slight increase in sample stiffness and the adhesive energy was bigger. This can be explained as resulting from an increase in the tackifier composition in the matrix *at the surface*. This stiffened the matrix and made it stickier. Further increases in the annealing temperature to 100°C and 150°C made the polymer-enriched matrix softer, probably due to polymer degradation by chain scission. Though a perfect PEP copolymer is quite stable to heating, residual double bonds in this material provides sites for scission. Thus, the behavior of the adhesive with aging results from a competition of two mechanisms, surface enrichment in tackifier that makes the surface stiffer and polymer degradation that makes it softer.

CONCLUSIONS

Morphological and frictional changes with time and temperature measured with scanning probe microscopy techniques indicate that as the adhesive ages at room temperature, the surface becomes more enriched in tackifier. With the tackifier-enriched phase being stiffer and covering the majority of the surface, this aging leads to a stiffer surface. At moderately elevated temperatures the same mechanism dominates. Thus, the performance of the adhesive, as measured by a test like nanoindentation, deteriorates with aging. When the adhesive surface becomes stiffer, the adhesive does not wet an adherend, affecting adversely the overall adhesive performance. Once more, this study highlights the capabilities of scanning probe microscopy techniques such as LFM and AFM for contributing to adhesion science by providing new and important information on a highly local scale.

Acknowledgements

The authors thank Professor R. P. Quirk, Dr. S. Corona-Galvan and Dr. R. S. Porzio for providing the polyisoprene, and Professor T. Kyu for useful discussions and for allowing us to use the hot stage. Research support from the Army Research Office, contracts DAAH04-95-1-0562 and DAAG55-97-1-0079 (DURIP), is gratefully acknowledged. S. Moon assisted in preparation of the figures.

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