

# Microscopic Stripe Formation and Adhesion Force Increase Introduced by Local Shear-Stress Deformation of Polypropylene Film

H.-Y. Nie,\* M. J. Walzak, B. Berno, and N. S. McIntyre

*Surface Science Western, The University of Western Ontario,  
London, Ontario N6A 5B7, Canada*

*Received February 17, 1999. In Final Form: May 19, 1999*

Localized shear deformation of biaxially oriented polypropylene (PP) film using a stylus force of 0.4 mN results in a reorientation of polymer strands in the shear-force direction, which appears as a striped region. This change in surface structure, which was observed by atomic force microscopy (AFM), resulted in an increase in the adhesion force as determined from the interaction between the AFM tip and the sample surface. This increase in adhesion force results from an increase in surface energy, which is thought to be caused by an increase in density and closer ordering of the polymer strands on the film surface. We demonstrate that the surface energy of PP film can be increased either by this mechanical scratching on the surface or by adding oxidation-induced chemical functional groups to the surface. The increase in surface energy from mechanical scratching of the PP surface is comparable to that introduced by surface oxidation of the unscratched PP surface after 1-min UV/ozone exposure.

## Introduction

Wettability of polymer surfaces is determined, in part, by the surface energy, which is the reversible work per unit area needed to create a new surface.<sup>1</sup> Because of its low surface energy, polypropylene (PP) film usually needs to be modified to increase its surface energy by plasma, flame, UV/ozone, and other treatments<sup>2</sup> for improved printability and adhesion. We have investigated UV/ozone modification of PP film<sup>3,4</sup> using various analytical techniques, including atomic force microscopy (AFM).<sup>5</sup> The later technique uses a cantilever to sense the interaction between the surface and the tip which is attached to the free end of the cantilever, to study changes in morphology and adhesion properties caused by UV/ozone treatment.<sup>4</sup> The torsional movement of the cantilever during the scan of the tip across the surface provides information on the friction force between the tip and surface;<sup>6</sup> the change in force measured while bringing the tip into contact with the surface and retracting it from the surface, referred to as the force–distance curve, provides information on adhesion forces<sup>4,7–11</sup> which can be related to surface energy.

In this paper, using AFM, we show that mechanical scratching of the PP film can dramatically change the surface structure and result in a substantial increase in

its adhesion force. The PP film used already had “native” microscopically striped surface regions, which were probably introduced by shear-stress deformation during the film conversion processes. These stripes, characterized by a deformed surface structure and reoriented polymer strands, were superimposed on the “normal” surface of nanometer-scale fiberlike network structure. We demonstrate that such striped structures can be reproducibly created by mechanical stresses. On the basis of our AFM measurements of surface structure and adhesion force on the striped surface, we discuss a relationship between the surface structure change and surface energy increase observed on such mechanically created striped regions. We demonstrate that the surface energy increase caused by mechanical scratching is related to changes in the density and ordering of polymer strands on the surface.

The mechanically scratched surface demonstrates an adhesion force increase comparable to that of a “normal” (unscratched) PP surface treated with UV/ozone for 1 min. While the latter increase in surface energy on such oxidized surface is due to the addition of polar chemical functional (e.g., carbonyl and hydroxyl) groups,<sup>3,4</sup> mechanical scratching provides an alternative physical method to modify local surface energy on the surface. Moreover, the scratches appear to undergo greater oxidative changes than the surrounding “normal” network structure when exposed to UV/ozone, which indicates that the scratches are more susceptible to greater increase in surface energy than the “normal” surface.

## Materials and Methods

Thermally extruded, biaxially oriented isotactic PP film (0.3 mm thick) was used in this study. The PP film was produced from a homopolymer resin (molecular weight  $M_w = 1.9 \times 10^5$ , polydispersity = 6.0). The base resin contains 500–1000 ppm each of an inorganic acid scavenger and a high-molecular-weight phenolic antioxidant. The PP was produced on a tenter frame film line and quenched at 45 °C prior to orientation. The machine direction draw ratio was 5.2:1, and the transverse direction draw ratio was 9:1. The film was converted in a direction identical to the machine direction.

Local mechanical stresses (“scratches”) were created using a stylus-type surface profiler (P-10, Tencor), in which a tip with

- (1) Cammarata, R. C. *Progr. Surf. Sci.* **1994**, *46*, 1.
- (2) Strobel, M.; Walzak, M. J.; Hill, J. M.; Lin, A.; Karbasheski, E.; Lyons, C. S. *J. Adhesion Sci. Technol.* **1995**, *9*, 365.
- (3) Walzak, M. J.; Flynn, S.; Foerch, R.; Hill, J. M.; Karbasheski, E.; Lin, A.; Strobel, M. *J. Adhes. Sci. Technol.* **1995**, *9*, 1229.
- (4) Nie, H.-Y.; Walzak, M. J.; Berno, B.; McIntyre, N. S. *Appl. Surf. Sci.* **1999**, *144–145*, 627.
- (5) Binnig, G.; Quate, C. F.; Gerber, Ch. *Phys. Rev. Lett.* **1986**, *56*, 930.
- (6) Meyer, G.; Amer, N. *Appl. Phys. Lett.* **1990**, *57*, 2089.
- (7) Mizes, H. A.; Loh, K.-G.; Miller, R. J.; Ahuja, S. K.; Grabowski, E. F. *Appl. Phys. Lett.* **1991**, *59*, 2901.
- (8) Radmacher, M.; Fritz, M.; Cleveland, J. P.; Walters, D. A.; Hansma, P. K. *Langmuir* **1994**, *10*, 3809.
- (9) Toikka, G.; Hayes, R. A.; Ralston, J. *J. Colloid Interface Sci.* **1996**, *180*, 329.
- (10) van der Vegte, E. W.; Hadziioannou, G. *Langmuir* **1997**, *13*, 4357.
- (11) Feldman, K.; Tervoort, T.; Smith, P.; Spencer, N. D. *Langmuir* **1998**, *14*, 372.

a radius of  $2.5 \mu\text{m}$  was used to scan the film surface at a scan speed of  $400 \mu\text{m/s}$  and a loading force of  $0.4 \text{ mN}$ . X-ray photoelectron spectroscopy (XPS) was used to determine if oxygen was introduced on the scratched surface.

The surface energy of the PP could be changed by exposing the PP film to ozone flow ( $2 \times 10^{17} \text{ molecule/cm}^3$ ) in the presence of UV radiation with primary lines at  $184.9$  and  $253.7 \text{ nm}$ . Atomic oxygen formed from the photodecomposition of ozone is believed to cause functionalization and eventual scission of PP chains.<sup>3</sup>

Both contact and (or dynamic) modes of a commercial AFM (Explorer, TopoMetrix) were employed. Contact mode AFM was used to measure the friction forces and force–distance curves. A soft cantilever with a sharp tip on its free end was used to detect the interaction between the tip and sample surface. The V-shaped silicon nitride cantilever had a nominal spring constant of  $0.03 \text{ N/m}$ . The cantilever was  $0.6 \mu\text{m}$  thick,  $18 \mu\text{m}$  wide, and  $200 \mu\text{m}$  long with a tip attached whose apex radius was  $\sim 20 \text{ nm}$ . In contact mode, the tip is mechanically in contact with the surface so that both the deflection and torsion of the cantilever can be determined by measuring the reflection of a laser light irradiated on the cantilever with a four-segment photodetector. The repulsive force (imaging force) between the tip and surface is kept constant by adjusting the sample height when scanning, and in this way, surface features are imaged. The imaging force of  $1\text{--}5 \text{ nN}$  did not degrade the PP film surface. During forward or reverse scanning of the tip on the surface, the torsion of the cantilever due to the interaction between the tip and surface can be used to detect different lateral forces which are used to construct the lateral force image. The direct output of the photodetector in units of  $\text{nA}$  was used to express the lateral force. The mathematical difference between bidirectional lateral force images eliminates offsets of the signals received by the photodetector and gives the friction force image.

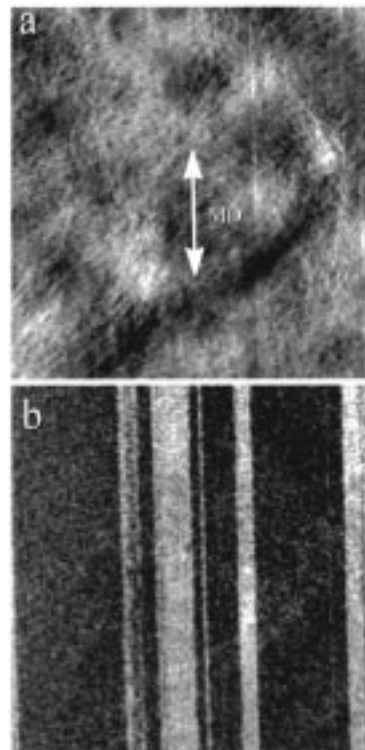
Noncontact mode AFM was used to measure topographic features of the surfaces. In noncontact AFM, a stiff silicon cantilever was used which was  $130 \mu\text{m}$  long,  $29 \mu\text{m}$  wide, and  $3.7 \mu\text{m}$  thick and the resonant frequency of this cantilever was  $\sim 280 \text{ kHz}$ . The tip apex radius was  $\sim 20 \text{ nm}$ . The noncontact AFM image was obtained through maintaining a constant oscillation amplitude of the cantilever while scanning the tip over the surface.

All images were obtained in air with a typical relative humidity of about 50%. Each image consisted of 500 lines with 500 pixel points per line. The scan rates for images of areas of  $1 \mu\text{m}$  square and over  $20 \mu\text{m}$  square were  $10$  and  $100 \mu\text{m/s}$ , respectively.

## Results

Figure 1 shows the contact mode AFM topographic (a) and friction force (b) images ( $20 \mu\text{m}$  square area) of the PP film surface. There are extremely faint, straight, striped regions oriented in the machine-draw (MD) direction (indicated by the insert arrow line). This image is expressed in gray scale with a height range of  $55 \text{ nm}$ , and the average height for the surface is  $24 \text{ nm}$ . The topographic height difference between the stripes and the "normal" surface is only  $1\text{--}2 \text{ nm}$ , which is much smaller than the roughness variation of the "normal" surface ( $\sim 9 \text{ nm}$ ). Therefore, the contrast between the stripes and "normal" surface is quite faint in Figure 1a.

In contrast to the faint difference in topographic features between the striped and "normal" surfaces, the friction force image shown in Figure 1b clearly identifies the striped regions on the basis of increased interaction with the tip. The friction force image is derived from the torsional movement of the cantilever induced by the interaction between the AFM tip and sample surface. Therefore, the contrast shown in Figure 1b indicates different surface properties between the striped and "normal" surfaces. This contrast can be explained by an increase of the interaction strength between the tip and surface as follows: the tip is held more strongly to the striped surface than the "normal" surface, resulting in a larger torsional movement of the cantilever when the tip

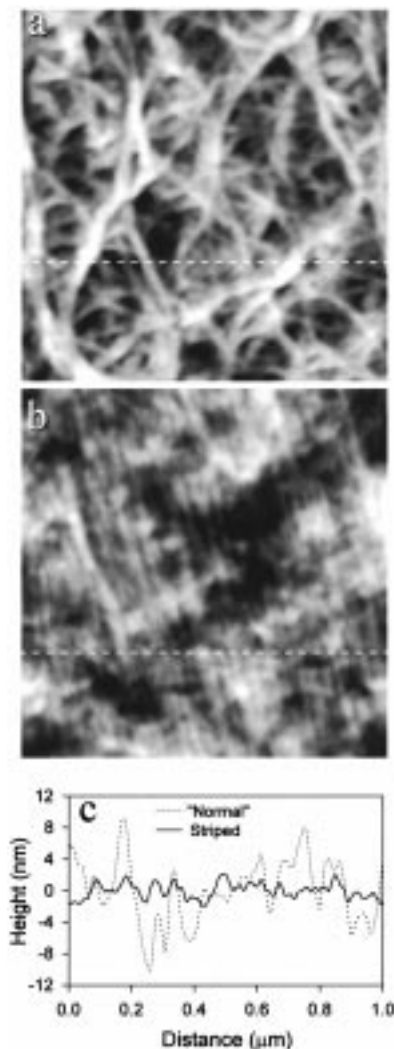


**Figure 1.** Contact mode AFM topographic (a) and friction force (b) images (scan area:  $20 \mu\text{m} \times 20 \mu\text{m}$ ) on a polypropylene (PP) film surface. The insert arrow line in (a) shows the machine-draw (MD) direction. The gray scale ranges in (a) and (b) are  $55 \text{ nm}$  and  $1.6 \text{ nA}$ , respectively. The friction force is expressed by the output of the photodetector corresponding to the torsion of the cantilever.

scans the surface. From measurements of many locations on the PP film, the width of striped regions seemed to range from  $0.2$  to  $3.0 \mu\text{m}$ . The striped region on the PP film was found to be exactly parallel to the MD direction, and the ends of the stripes were never observed. It was the friction force difference shown in Figure 1b that stimulated further investigation of the structure and properties of the striped surface on the PP film.

Typical noncontact AFM topographic images ( $1 \mu\text{m}$  square area) obtained on the "normal" and striped regions are shown in Figure 2a,b, respectively. Figure 2a shows that the "normal" surface is characterized by a nanometer-scale fiberlike network structure, which is the result of the sequential biaxial orienting process. Figure 2b shows that the striped surface has a totally different structure from the "normal" surface. Compared to the networklike fibers seen on the "normal" surface, on the striped region, there is a high degree of alignment of strands parallel to the MD direction. It is clear that the morphology shown in Figure 2b presents a trace of shear-stress deformation of the "normal" surface. Shown in Figure 2c are two representative cross section profiles obtained from the positions indicated by dashed lines inserted in Figure 2a,b, respectively. One sees that the corrugation height is much smaller on the striped surface (solid line) than on the "normal" surface (dashed line), which could be explained by the deformation of the fibers caused by the shear stresses.

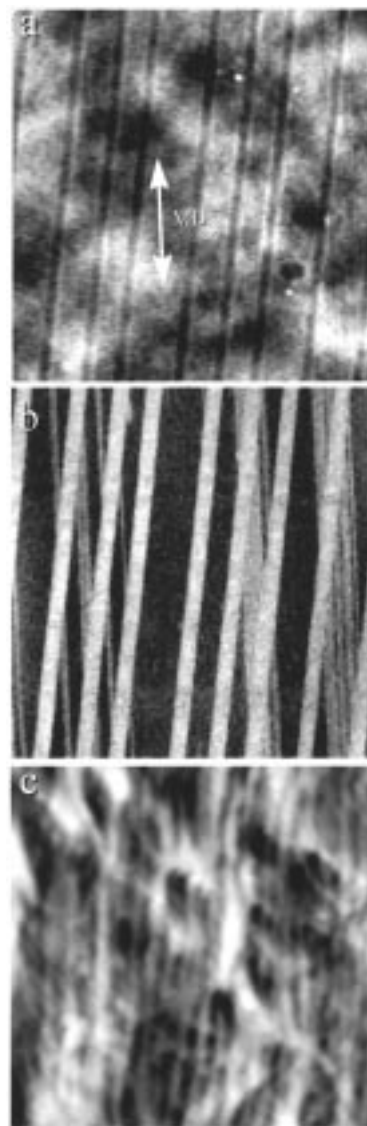
On the basis of the direction of the strands and the deformation of the surface observed in Figure 2, it is most likely that the striped regions are introduced by shear stress. Such striped surface structures could be reproducibly created by using a stylus-type profiler tip to "scratch" the PP film. To create stripes with a size



**Figure 2.** Noncontact mode AFM topographic images (scan area:  $1 \mu\text{m} \times 1 \mu\text{m}$ ) for “normal” (a) and striped (b) surfaces. Gray scale ranges for (a) and (b) are 21 and 11 nm, respectively. Shown in (c) are the cross section profiles for the “normal” (dashed line) and striped (solid line) surfaces obtained at the positions marked by insert dashed lines in the images of (a) and (b), respectively.

comparable to the “native” stripes, a tip with a radius of  $2.5 \mu\text{m}$  was scanned across the PP film surface using a stylus-type surface profiler with a loading force of 0.4 mN. Shown in Figure 3a is a contact mode AFM topographic image ( $35 \mu\text{m}$  square area) obtained on such a scratched PP film, in which the scratched stripes with a depth of several nanometers are visible. The scratched stripes were created  $\sim 10^\circ$  off from the MD direction shown by the insert arrow line. They appear much more clearly because they are more greatly deformed than the “native” stripes. There are nine stripes in this image, including the two respectively located at the left-upper and right-lower corners. The width of mechanically created stripes is related to the applied force; stripes  $0.2\text{--}2.5 \mu\text{m}$  wide were created by changing loading forces from 0.1 to 0.5 mN.

The friction force image obtained on the scratched PP film is shown in Figure 3b. In this image it is clear that the nine stripes have a much higher contrast than the “normal” surface. Some stripes were created on an area where the “native” scratches running in the MD direction existed. Shown in Figure 3c is a noncontact mode AFM image ( $1 \mu\text{m}$  square area) obtained on the scratched stripe

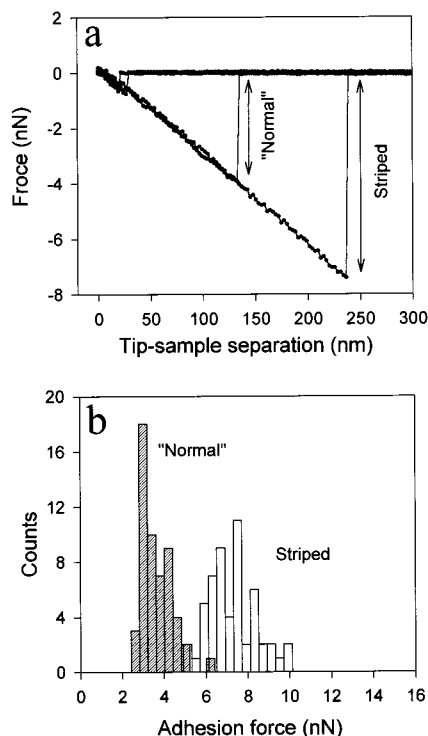


**Figure 3.** Contact mode AFM topographic (a) and friction force (b) images (scan area:  $35 \mu\text{m} \times 35 \mu\text{m}$ ) on a polypropylene (PP) film surface scratched by using a stylus-type surface profiler. The insert arrow line shows the machine-draw (MD) direction. Shown in (c) is a noncontact mode AFM topographic image (scan area:  $1 \mu\text{m} \times 1 \mu\text{m}$ ) on the scratched stripe surface. Gray scale ranges are 55 nm, 1.6 nA, and 11 nm for (a)–(c), respectively.

surface. It is clear that there are strands in alignment parallel to the scratching direction.

The scratching experimental result shown in Figure 3 indicates that the “native” stripes shown in Figure 1 were introduced by local shear-stress deformation in the film conversion process, in which the film was rolled through a number of rollers. Such deformation could easily occur if there were tiny protrusions on the rollers, which applied exceptional pressure to the running film.

To relate differences in the morphology and friction force between the “normal” and striped surfaces, we consider adhesion force changes measurable from the force–distance curve in AFM. Shown in Figure 4a are two representative force–distance curves obtained on the “normal” and scratched stripe surfaces. The same tip was used to complete the force–distance curve measurement within a short period of time. The tip was brought to the surface to make contact between the tip and the surface followed by retracting the tip from the surface. The original



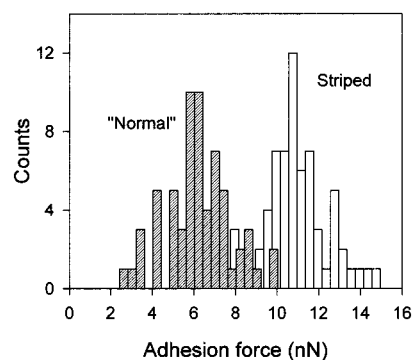
**Figure 4.** Two representative force–distance curves obtained on the “normal” and striped regions (a) and histograms (b) for the distribution of adhesion forces obtained from the force–distance curves. The two arrow lines in (a) indicate the adhesion forces for the “normal” and striped surface. The speed of the tip movement during force–distance curve measurement was  $1 \mu\text{m/s}$ .

point for the distance is defined as the mechanical contact between the tip and surface. In the retraction of the tip, because of the adhesion forces between the tip and surface, the tip will not depart from the surface until the force used to pull the tip from the surface exceeds the force that holds them together. This pull-off force can be considered as a measure of the adhesion force between the tip and surface.<sup>7–11</sup> As shown in Figure 4a, there is a clear difference in the adhesion force between the “normal” and striped surfaces.

The reproducibility of the difference in adhesion forces between the “normal” and striped surfaces was confirmed by repeating force–distance measurements on a number of locations at the two different surfaces. The distributions of adhesion forces for the “normal” and striped surfaces are summarized in the histograms shown in Figure 4b. The adhesion forces obtained on the “normal” and striped surfaces are  $3.8 \pm 0.7$  and  $7.4 \pm 1.1$  nN, respectively. It is clear that on the striped surface there is a remarkable increase in adhesion force.

A large area (1 mm square area) was scratched and analyzed by XPS for evidence of other related elements. None was found to a detection limit of 0.2%. It appears that the increase in adhesion force on the striped surface is not due to reactions with other elements such as oxygen.

It is known that when PP film is treated with UV/ozone for over 3 min, there is an increase in adhesion force and formation of mounds/droplets on the surface;<sup>4</sup> this is attributed to surface functionalization as well as the formation of low-molecular-weight oxidized materials.<sup>3</sup> After a 1-min UV/ozone treatment, there was a barely detectable change in morphology, but the adhesion force estimated from force–distance curves showed a substantial increase. The results of the adhesion forces obtained



**Figure 5.** Histograms for adhesion forces obtained from the force–distance curves measured at the “normal” and striped surfaces treated by UV/ozone exposure for 1 min. The speed of the tip movement during force–distance curve measurement was  $1 \mu\text{m/s}$ .

on the “normal” and striped surfaces of the 1-min treated PP film are summarized in the histograms shown in Figure 5. The adhesion force on the “normal” surface, the adhesion force was found to be increased to  $6.4 \pm 1.5$  nN. The 1-min UV/ozone treated PP film shows a clear increase in adhesion forces on both the “normal” and striped surfaces, compared to the histograms for the untreated PP film shown in Figure 4b. The tip used to obtain adhesion forces shown in Figure 5 was the same one used for Figure 4.

After this 1-min UV/ozone treatment, oxygen was clearly detected by XPS on both the “normal” and striped surfaces. Therefore, the adhesion force increase shown in Figure 5 is likely due to a formation of oxidation-induced (chemical functional) groups caused by UV/ozone treatment. Our result indicates that the UV/ozone treatment modifies the chemical properties at short treatment times.

## Discussion

Surface energy, the excess free energy due to the existence of a surface,<sup>1</sup> is a measure of degree of chemical reactivity of the surface. To relate surface energy and morphology change observed in our AFM measurement on mechanically scratched PP films, we first discuss the relationship between the adhesion force, as estimated from the force–distance measurement, and the surface energy. The adhesion force between two bodies in contact can be related to their surface energies and the interfacial energy between them. Assuming the curvature of the sample surface is much larger than the apex radius  $R$  of the AFM tip, the Johnson–Kendal–Roberts theory indicates that the adhesion force  $F$  between them is related to the work of adhesion  $w$  (or interaction energy),<sup>12</sup>

$$F = -(3/2)\pi R w \quad (1)$$

The work of adhesion can be generally related to surface energies of the sample  $\gamma_1 = \gamma_1^d + \gamma_1^p$  and tip  $\gamma_2 = \gamma_2^d + \gamma_2^p$ , where superscripts d and p denote dispersion and polar (nondispersion) components of the surface energy, respectively. It is commonly accepted that the geometric mean of the dispersion components of the surface energies describes well the dispersion part of the work of adhesion,  $w^d = 2(\gamma_1^d \gamma_2^d)^{1/2}$ .<sup>12</sup> An analogy of the geometric mean rule for the polar component of the work of adhesion,  $w^p = 2(\gamma_1^p \gamma_2^p)^{1/2}$ ,<sup>13–18</sup> is useful here to see the relationship

(12) Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed; Academic Press: London, 1991.

(13) Owens, D. K. *J. Appl. Polym. Sci.* **1970**, *14*, 1725.

(14) Good, R. J. *J. Colloid Interface Sci.* **1977**, *59*, 398.

between the adhesion force and surface energy. The total work of adhesion can thus be expressed as the following:<sup>16–18</sup>

$$w = w^d + w^p = 2(\gamma_1^d \gamma_2^d)^{1/2} + 2(\gamma_1^p \gamma_2^p)^{1/2} \quad (2)$$

It is likely that under our experimental conditions the surface energy of the tip  $\gamma_2$  remained unchanged during the measurement. Hence, eqs 1 and 2 indicate that an increase in the adhesion force is due to an increase in the sample surface energy. From the adhesion force difference measured between the striped and “normal” surface (Figure 3), it is clear that the striped surface has a higher surface energy than the “normal” surface.

In ambient air, it is commonly believed that there is a condensed water film formed on materials with high surface energy, such as mica (120 mJ/m<sup>2</sup>)<sup>15</sup> and many metals (400–4000 mJ/m<sup>2</sup>).<sup>12</sup> This wetting process on a surface (or the wettability of the surface) is mainly determined by the surface energy. Capillary force may arise in the force–distance measurement through a formation of liquid bridge between the condensed layer and the AFM tip after the contact of the two. Because the surface energy of PP is usually low, e.g.,  $\sim 30$  mJ/m<sup>2</sup>,<sup>19–21</sup> it is unlikely that there is water film condensed on our PP film. Even if there is a formation of condensed layers on the PP film surface and they contribute to the measured adhesion force, a higher capillary force should imply a higher surface energy for a PP film with different surface structures (i.e., “normal” and striped surfaces). Therefore, whether a capillary force contributed to the measured adhesion force, there is evidence of surface energy changes between the striped and “normal” surfaces. It is this surface energy change that allows the friction force image to reveal a clear contrast between the “normal” and striped surfaces as shown in Figures 1b and 3b. It is, therefore, clear that AFM can be used to distinguish qualitatively local distribution of surface energy.

From the above discussion on the relationship of adhesion force and surface energy, we can see that there is an increase in surface energy on the mechanically scratched stripe surface as estimated from the force–distance curve measurements (Figure 4). The surface energy for a certain material is decided by the nature of intermolecular force<sup>12</sup> which makes molecules cohesive. For PP, which is a nonpolar polymer, molecular cohesion is maintained by dispersion forces.<sup>22</sup> The fiberlike network structure of the “normal” surface shown in Figure 2a is due to stretching of polymer in two (MD and TD) directions. This “normal” surface structure is considered to be in an equilibrium state of polymer strands, which should represent the minimum surface energy for the PP film. It is apparent that changes in surface structure can result in a change in surface energy.

The striped surface has experienced a localized shear stress that deformed the “normal” surface and resulted in

a formation of a different surface where there is no longer a fiberlike network structure, but strands appear with a certain alignment in the shearing direction. Because the striped surface is apparently deformed by the shear stress, which can be seen in Figure 2, the density of polymer strands on the striped surface is likely increased. Moreover, on the stripes the polymer strands show an increase in degree of directional ordering (see Figure 3), i.e., single direction for the striped surface vs multidirection (network) for the “normal” surface. This represents an increase in the ordering and density of polymer strands on the striped PP film surface caused by mechanical forces. These would inevitably increase surface energy because dispersion forces<sup>12</sup> between molecules need to be increased to maintain a more “compressed” and “ordered” striped surface structure compared to the “normal” surface. The cost for the observed increase in surface energy of the deformed and reoriented polymer strands on the surface seen in Figures 2b and 3c comes from part of the work done by the mechanical scratching.

Having discussed the mechanism for the surface energy increase caused by increase in density and ordering of surface polymer strands, we also note that there is another case for surface energy increase on the PP film: the adding of chemical functional groups and/or oxidized materials having higher surface energy to the polymer. Such surface modification has been reported previously, in which, for example, adhesion force increase and droplet formation on the PP film treated by UV/ozone for 15 min were observed.<sup>4</sup> For the 1-min UV/ozone treatment presented in the present study, the oxidation is not enough to cause apparent change in PP film surface morphology. On the basis of the fact that the uptake of oxygen on the 1-min UV/ozone treated PP film is clearly detected by XPS and there is an increase in adhesion force (compare Figures 4b and 5), there is evidence for a formation of chemical functional groups on the surface. PP film has inherently low surface energy because of low intermolecular (dispersion) forces between molecules. It is polar groups and/or oxidized materials introduced on the surface in the oxidation of the PP film that increase the surface energy.

A notable experimental fact extracted from Figures 4b and 5 is, therefore, that the surface energy increase caused by the mechanical scratching is comparable to that caused chemically by the UV/ozone treatment for 1 min. This experiment fact indicates that mechanical scratching can be an alternative for creating active surface or improving wettability on polymer surface. The advantage of this mechanical alternative for surface modification using AFM lies in its ability to modify surface locally on a nanometer scale by choosing appropriate stylus tips and loading forces.

From the adhesion force measurement results shown in Figure 5, one can also see that the adhesion force increase on the striped surface is larger than that on the “normal” PP film surface, i.e., 3.7 nN vs 2.6 nN. This difference in the increase of adhesion force (surface energy) between the striped and “normal” surfaces indicates that the scratched areas are more susceptible to further increase in surface energy using UV/ozone treatment. This result is considered as evidence for the higher surface energy on the mechanically scratched PP film surface; i.e., a surface with higher surface energy is more reactive.

## Conclusions

Through an AFM study of mechanically scratched surface structures on biaxially oriented polypropylene films, we established that such structures are unique for

(15) Schultz, J.; Tsutsumi, K.; Donnet, J. D. *J. Colloid Interface Sci.* **1977**, *59*, 277.

(16) Gutowski, W. In *Fundamentals of Adhesion*; Lee, L. H., Ed.; Plenum Press: New York, 1991; p 87.

(17) Schultz, J.; Nardin, M. In *Handbook of Adhesive Technology*; Pizzi, A., Mittal, K. L., Eds.; Marcel Dekker: New York, 1994; p 19.

(18) Garbassi, F.; Morra, M.; Occhiello, E. *Polymer Surface-From Physics to Technology*; John Wiley & Sons: Chichester, U.K., 1994; p 161.

(19) van Oss, C. J.; Chaudhury, M. K.; Good, R. J. *Sep. Sci. Technol.* **1989**, *24*, 15.

(20) Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982; Chapter 5.

(21) Schonhorn, H.; Sharpe, L. H. *J. Polym. Sci. B* **1965**, *3*, 235.

(22) Stevens, M. P. *Polymer Chemistry: an Introduction*, 3rd ed.; Oxford University Press: New York, 1999; Chapter 3.

relating changes of surface morphology and surface energy. Reorientation of surface polymer strands by the shear stress was observed using high magnification AFM images, and the surface energy increase in the area of reorientation was distinguished by friction force imaging and related to the adhesion force increase measured using force-distance curves. The observed surface energy increase on the mechanically scratched surface is proposed to be due to a buildup of an extra free energy, which is from part of the work done by the mechanical-scratching, in increasing density and in the ordering of polymer strands on the deformed surface. We demonstrated that this physical modification of surface energy by mechanical

scratching is different from the increase in surface energy by UV/ozone treatment, which induces chemical functional groups on the surface through the oxidation of the surface. Being able to change the surface energy of a polymer surface locally by mechanical scratching without changing the surface energy of the surrounding polymer and without influencing the bulk properties of the polymer has implications in a number of fields including creating *local* active sites on surface in terms of surface energy increase or wettability improvement.

LA990166H