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.

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,3,4 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 of an inorganic acid scavenger and a high-molecular-weight phenolic antioxidant. The PP was produced on a tenter frame filmline 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...
a radius of 2.5 μm was used to scan the film surface at a scan speed of 400 μm/s and a loading force of 0.4 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 × 10¹⁷ molecule/cm²) in the presence of UV radiation with primary lines at 184.9 and 253.7 nm. Atomic oxygen formed from the photodecomposition of ozone is believed to cause functionalization and eventual scission of PP chains.

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 N/m. The cantilever was 0.6 μm thick, 18 μm wide, and 200 μm long with a tip attached whose apex radius was ~20 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 1–5 N 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 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 μm long, 29 μm wide, and 3.7 μm thick and the resonant frequency of this cantilever was ~280 kHz. The tip apex radius was ~20 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 μm² and over 20 μm² were 10 and 100 μm/s, respectively.

Results

Figure 1 shows the contact mode AFM topographic (a) and friction force (b) images (20 μm × 20 μm) on a polypropylene (PP) film surface. The insert arrow line in (a) shows the machine-drawn (MD) direction. The gray scale ranges in (a) and (b) are 55 nm and 1.6 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 μm. 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 μm 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 stripes 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
comparable to the “native” stripes, a tip with a radius of 2.5 μm 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 μm 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 ~10° 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 0.2–2.5 μm 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 μm square area) obtained on the scratched stripe 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
The adhesion forces obtained on the "normal" and striped surfaces are 3.8 and 7.4 \( \mu \text{N} \), respectively. It is commonly accepted that the geometric mean rule of the geometric mean rule of Johnson–Kendall–Roberts theory indicates that 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 of the AFM tip, the Johnson–Kendall–Roberts theory indicates that the adhesion force \( F \) between them is related to the work of adhesion \( w \) (or interaction energy),

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F = -(3/2)\pi R w
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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 (nonpolar) components of the surface energy, respectively. It is commonly accepted that the geometric mean of the dispersion components of the surface energy describes well the dispersion part of the work of adhesion, \( \gamma^0 = 2(\gamma_1^d\gamma_2^d)^{1/2} \). An analogy of the geometric mean rule for the polar component of the work of adhesion, \( \gamma^p = 2(\gamma_1^p\gamma_2^p)^{1/2} \), is useful here to see the relationship

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\gamma^0 = 2(\gamma_1^d\gamma_2^d)^{1/2}
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\gamma^p = 2(\gamma_1^p\gamma_2^p)^{1/2}
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(14)\text{Good, R. J. J. Colloid Interface Sci. 1977, 59, 398.}
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between the adhesion force and surface energy. The total work of adhesion can thus be expressed as the following: \[ w = w^d + w^l = 2\gamma_{12}^d + 2\gamma_{12}^p + \frac{1}{2}\gamma_{22} \] (2)

It is likely that under our experimental conditions the surface energy of the tip \( \gamma_{22} \) 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\(^2\)) and many metals (400–4000 mJ/m\(^2\)).\(^{12}\) 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., ~30 mJ/m\(^2\),\(^{19,21}\) 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 the 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 forces\(^{12}\) which makes molecules cohesive. For PP, which is a nonpolar polymer, molecular cohesion is maintained by dispersion forces.\(^{22}\) The “normal” surface structure 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 structure can result in a change in surface energy.

The striped surface has experienced a localized shear strain 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, 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\(^{12}\) 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.\(^4\) 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, 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.

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