# AFM Studies of Corona Treated Biaxially Oriented PET Film

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## ABSTRACT

A sixteen run designed experiment was performed on biaxially oriented PET film with line speed and corona treater power setting as variables. The corona treater gap was held constant. Using Atomic Force Microscopy (AFM), surface topography and compositional variations were measured on each sample of treated film. Surface roughness values, Ra, were determined from the AFM images. The surface energy of each sample was obtained from contact angle data immediately after production. Each sample was also aged at 50°C for one week and then imaged with AFM again to determine any changes in roughness or composition. The film was washed with deionized water to remove any water soluble low molecular weight material formed in the corona treatment. The material was analyzed with mass spectroscopy and nuclear resonance spectroscopy in an effort to identify the material(s). Comparisons will be made between these results and our prior results of corona treatment of uniaxially oriented PET film.

## INTRODUCTION

Corona treatment has been used routinely to improve adhesion and surface wettability of polymer surfaces [1-4]. Converters have used corona treatment to produce constructions that have improved ink and lamination adhesion. This method has been regularly used for many years in the packaging industry as well as other markets.

During corona discharge treatment of poly(ethylene terephthalate) (PET) films the surface is partially oxidized to yield an increase in the quantity of oxygen containing functional groups as well as small amounts of nitrogen containing materials [5-7]. This process results in increased surface energy which enhances printing as well as self adherence. Soluble, low molecular weight materials have been reported as products of various treatment levels on biaxially oriented films of several polymer types presumably by chain scission [1,5,7,8]. These prior researchers have used a combination of spectroscopic tools to elucidate the types of oxidized functional groups that are produced during corona treatment.

The advent of scanning probe microscopy techniques has given rise to nanometer scale resolution of polymeric film surfaces. Using atomic force microscopy (AFM), surface topography as well as variations in surface composition can be determined. This AFM study was designed to evaluate the surface changes produced by corona treatment under a variety of conditions with biaxially oriented PET. In our previous work, uniaxially oriented forward drawn sheet (FDS) was examined using varying line speed, corona power setting and gap between the FDS and the treater bars [9].

In this study unfilled, virgin PET was used to prepare biaxially oriented samples on a pilot scale film line where line speed and corona treater power levels were varied. Both corona treater gap and film thickness were held constant in this study. The biaxially oriented samples provide a picture of the surface of the film that would typically be used in converting steps. The results obtained from this study are presented below. These results using biaxially drawn PET film are consistent with the previous study on uniaxially draw sheet.

## EXPERIMENTAL

### PET Film Sample Preparation

Biaxially oriented film samples were prepared on the R&D pilot film line at Mitsubishi Polyester Film, Inc. An ENERCON corona treater with two 1.292 ft bars was used for in-line treatment on the air side of the film. The experiment used two input variables: line speed and corona treater power setting. This led to the construction of a 15 run experiment. One control sample was added to produce an experiment of 16 runs as indicated in Table 1. The resulting watt-density (WD) is calculated for each sample from WD= power/(line speed*bar length) and is included in Table 1 for reference.

**Table 1: Experiment Variables.**

| Run | Line Speed (ft/min) | Corona Power (kW) | Watt-density (W-min/ft$^2$/min) |
|---|---|---|---|
| 0 | 0.0 | Off | 0.0 |
| 1 | 40 | 0.3 | 5.80 |
| 2 | 40 | 0.5 | 9.67 |
| 3 | 40 | 0.7 | 13.54 |
| 4 | 75 | 0.3 | 3.10 |
| 5 | 75 | 0.5 | 5.16 |

| | | | |
|---|---|---|---|
| 6 | 75 | 0.7 | 7.22 |
| 7 | 100 | 0.3 | 2.32 |
| 8 | 100 | 0.5 | 3.87 |
| 9 | 100 | 0.7 | 5.42 |
| 10 | 150 | 0.3 | 1.55 |
| 11 | 150 | 0.5 | 2.58 |
| 12 | 150 | 0.7 | 3.61 |
| 13 | 200 | 0.3 | 1.16 |
| 14 | 200 | 0.5 | 1.93 |
| 15 | 200 | 0.7 | 2.71 |

**Atomic Force Microscopy**

Portions cut from the center of the film samples were mounted on 15 mm diameter metal discs using 3M Scotch-Weld 2216 B/A Gray Epoxyadhesive tabs immediately after production. In order to obtain pristine surfaces for analysis the FDS sample surfaces were not allowed to contact anything prior to analysis. AFM images were obtained using TappingMode® in air with phase imaging (Micromasch Ultrasharp NSC15/AlBS tips) on a Veeco Dimension 3100MultiMode microscope with a Nanoscope IV IIIa controller using Nanoscope Version 6.11r1 software. To ensure reproducibility of the data all images were obtained using identical scan conditions: a scan rate of 1.97 Hz, a ratio of set-point amplitude oscillation to free amplitude oscillation, Rsp, of 0.80, and integral and proportional feedback gains of 0.10 and 0.20 respectively. For each sample multiple 10 x 10 µm, 5 x 5 µm, and 2 x 2 µm images were recorded. Version 5.12r3 of the Nanoscope software was used to perform a 2$^{nd}$ order flattening of each image and to determine the surface roughness. Average surface roughnesses, Ra, were calculated for each film sample using the 5 µm images and then using the 2 µm images.

**Surface Energy Measurements**

Contact angles were measured using a VCA 2500XE video contact angle system (AST Products). Both the right and left contact angles for a minimum of three drops of deionized water placed on the surface via microsyringe were analyzed for each sample. The surface energy was calculated from Equation 1 using the average contact angle, , in degrees. The surface tension of a drop of deionized water was verified to be 72.2 dynes/cm prior to each set of measurements. Contact angles were measured within 24 hrs of production.

**Equation 1**  $Surface\ Energy = \frac{1}{2}(1 + \cos\theta)(72 - \frac{\theta}{8})$

**RESULTS AND DISCUSSION**

**AFM Characterization of PET Film Samples**

An experiment was constructed to evaluate the variables contributing to overall surface changes upon corona treatment of biaxially oriented polyethylene terephthale (PET) film. Film samples of each of the 16 runs were prepared on the pilot line using unfilled, virgin PET. Since it was of interest to see what these surfaces looked like immediately after corona treatment a portion of each sample was immediately mounted for AFM analysis. In contrast to other studies, the samples were carefully collected immediately after corona treatment in a manner that prevented them from ever coming in contact with any other PET surfaces, as opposed to a rolled or a slab sample.

AFM images were obtained for each sample using constant scan conditions in order to determine the surface roughness of each set of corona treater conditions. In order to acquire reproducible roughness values of polymer surfaces it is imperative that the strength of tapping, Rsp, as well as the scan size and scan rate be held constant. Throughout these AFM experiments an Rsp of 0.80 was used, which represents a medium tapping regime. As the samples at each line speed were imaged varying amounts of relatively mobile material were detected on the surfaces.

As shown in Figures 1, an increase in the watt-density used in the corona treatment increased the amount of the mobile material that was detectable in the image pairs. Each image pair in these figures is composed of a topographical image, left side, and a phase image, right side, with the color variation reflecting differences in height in the topographical image or differences in phase composition in the phase image. The mobile material was always detected as a raised feature in the topography image
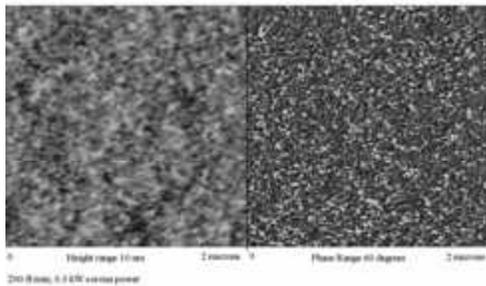
**Figure 1. 2x2 µm AFM images of film samples run at constant line speeds and varying the watt density with the topographical image on the left, height range 10 nm, and the phase image on the right, phase range 60°, in each image pair. a) no corona treatment, b) WD = 1.16 W/ft$^2$/min, c) WD = 1.93 W/ft$^2$/min, d) WD= 2.71 W/ft$^2$/min.**
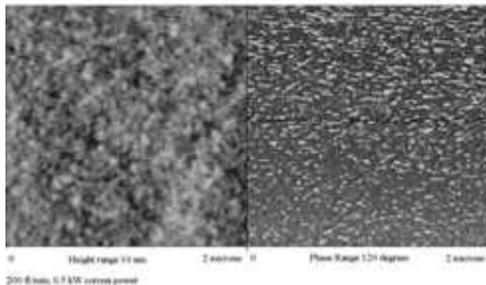
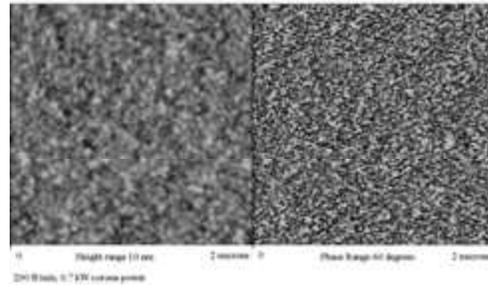Formatted: Font: 10 pt, Bold, English (U.S.)

**a)**
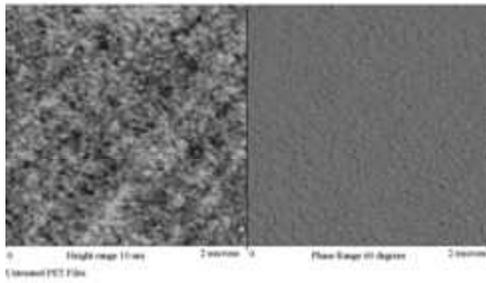


**b)**



**c)**



**d)**



It is also apparent that the line speed influenced the relative amount of this material. A comparison of images a and b in Figure 2 shows that with the same corona treaterd power at varying line speed significantly more material is generated at slower speeds.

**Figure 2. 2x2 µm AFM images of film samples run at varying line speeds and a constant treater power setting with the topographical image on the left, height range 10 nm, and the phase image on the right, phase range 60°, in each image pair. a) 200 ft/min, 0.3 kW, WD = 1.16 W/ft$^2$/min; b) 100 ft/min, 0.3 kW, WD = 2.32 W/ft$^2$/min.**

**a)**
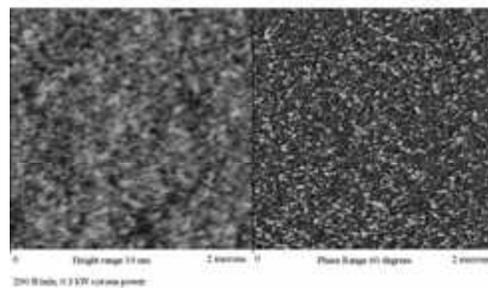
**b)**
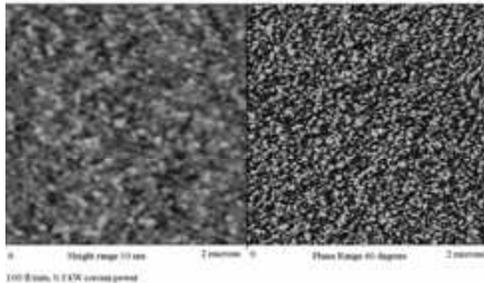


**Surface Roughness of Corona Treated PET Film**

Average surface roughnesses, Ra, were calculated for each of the samples using the routine provided in Version 5.12r3 of the Nanoscope software. This allowed for a more quantitative analysis of the relative amount of deposited material. The roughness data is summarized in Table 2.

As expected, the calculated roughness values increased as the amount of observable mobile material increased. The surface roughness remained relatively constant until a watt-density of approximately 6 $W/ft^2/min$ was reached, at which point it began to increase and become more variable as shown in Figure 34.

The correlations were most apparent when the Ra values from the 2x2 µm AFM images were evaluated. The 5x5 µm images occasionally had random larger features which gave more spread to the calculated Ra values. Generally, a decrease in line speed increased the roughness as did an increase in the corona power level.

**Table 2. Roughness and Surface Energy Data**

| Line Speed ft/m | Watt Density $W/ft^2/min$ | Surface Energy, dynes/cm | Ra, nm 5µm images | Ra, nm 2µm images |
|---|---|---|---|---|
| 40 | 0.0 | 43.9 | 0.458 | 0.529 |
| 40 | 5.80 | 56.5 | 0.774 | 0.530 |
| 40 | 9.67 | 57.7 | 0.444 | 0.887 |
| 40 | 13.54 | 57.5 | 0.995 | 0.784 |
| 75 | 3.10 | 54.5 | 0.562 | 0.526 |
| 75 | 5.16 | 57.2 | 0.930 | 0.485 |
| 75 | 7.22 | 58.1 | 0.585 | 0.626 |
| 100 | 2.32 | 52.4 | 0.551 | 0.508 |
| 100 | 3.87 | 58.8 | 0.572 | 0.495 |
| 100 | 5.42 | 57.6 | 0.632 | 0.428 |
| 150 | 1.55 | 52.3 | 0.541 | 0.580 |
| 150 | 2.58 | 55.4 | 0.525 | 0.491 |

**Figure 23. Surface roughness vs. watt-density plots for the 2x2 micron images.**
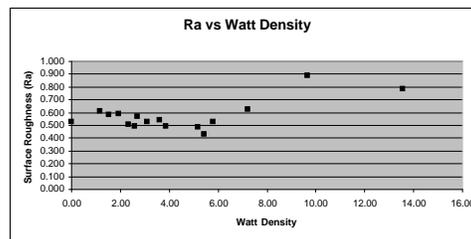


**Surface Energies**

In addition to producing the film samples used for AFM characterization, additional samples were collected for surface energy determinations.

All of the treated samples showed the increase in surface energy expected for corona treated PET. The surface energy showed a general increase until the watt-density reached approximately 4 $W/ft^2/min$ as seen in Figure 4. At this point the surface energy leveled off at a value of approximately 58 dynes/cm. At these higher watt-densities the surfaces are substantially coated with low molecular weight oxidized materials, LMWOM. It is important to realize that the presence of the LMWOM can influence the accuracy of the surface energies measurements. Since the material was water soluble, the surface tension of the water drops used in the surface energy determinations would be altered as the material quickly dissolved into them. The method used for calculating the surface energy assumes that the drop is pure water. Since it is a droplet of variable concentration of LMWOM care must be taken when directly comparing the values obtained.

**Figure 4. Surface energy vs Watt Density**

**Surface Deposit Characterization**

In our previous study, it was determined that this mobile material was mostly water soluble.

Figure 35 shows AFM images before and after washing a heavily treated sample with deionized water. The sample was imaged and then rinsed three times with 100 µl of DI water. Prior to rinsing the raised features of the mobile material was clearly visible. After washing, the raised features were gone and the surface showed ridges and pitting due to the corona treatment. Samples with large amounts of deposited material showed many ridges and pits while samples displaying only small amounts of deposited material showed fewer ridges and pits after washing with water. The corona treatment apparently roughens the surface by sputtering material off of the sample. Varying proportions of this sputtered, lower molecular weight material then resettles on to the surface.

**Figure 53. Topographical AFM images of the 40 ft/min line speed sample with WD=5.8 W/ft$^2$/min, 5x5 micron with a height range of 10 nm, a) before washing, b) after three washes with deionized water, and the untreated control**
**a)**



**b)**



**c)**



Analogous observations have been reported for biaxially oriented PET films [7], polypropylene films [109-110], and polyethylene films [121]. O'Hare reported that regardless of treatment level or line speed, biaxially oriented PET films subjected to off-line corona treatment incorporate phenolic-OH, carbonyl, and carboxylic acid residues on the surface after corona treatment [7]. These new functional groups were present before and after washing with a 50-50 methanol-water mixture although the total oxygen content of the surface, as determined by XPS, decreased after washing. O'Hare also proposed that the shape of the raised deposits was due to a difference in surface energy of the LMWOM and the PET surface. If it is the presence of these LMWOM that increases the mechanical and adhesion levels, varying the corona treatment level on film will alter these properties significantly.

Since most converters will store PET film before use what happens to corona treated film when stored in a warehouse is of interest. It is well know that stored, corona treated PET film will lose surface energy over time. In an effort to simulate this effect, the surface

roughness was ~~run~~ determined before and after storage of the samples at 50°C for 7 days.  The high temperature was intended to simulate long term storage in a warehouse. The results are shown in Figure 6.  ~~The is~~This indicates that over the course of the experimental parameters, not much change occurs.  Generally, the surface roughnesses ~~s~~ were ~~slightly~~ very similar

We know that corona treated film shows a decrease in surface energy over time.   This affect is shown in Figure 7.  PET film that has been corona treated generally has a surface energy level >53 dynes.  After storage for several months the surface energy can be reduced to the high 40's and with very long storage times the surface energy should approach the surface energy of untreated PET film (~42-43 dynes).

For the decrease in surface energy there must be a change at the surface.   It is possible that the LMWOM is absorbed into the film surface.   This may explain the decrease in surface energy seen over time.

~~In addition,~~Also  the resulting phenolic, carbonyl, etc. species produced will also have to be absorbed into the bulk film yielding a surface that resembles untreated PET film.

**Figure 6.   2x2 µm AFM images of film samples showing the surface roughness before and after heating the samples.**
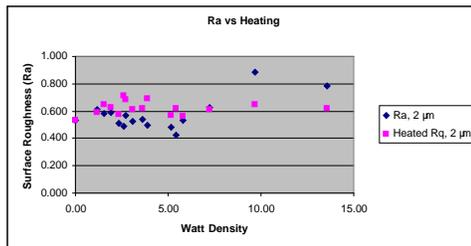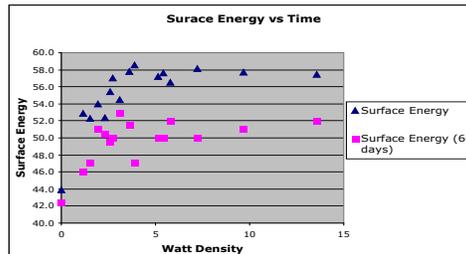


**Figure 7.  Surface Energy of initial samples and samples stored for 60 days compared to initial samples**



In addition to the AFM imaging of the film surfaces after corona treatment, collection of the LMWOM was done and a characterization was attempted.

Collection of the mobile material was done immediately after the corona treatment process (high watt density) by means of  ~~a~~ film washing~~station~~.   Analysis is not yet complete.  ~~Deionized water was used to wash the film which yielded a yellow-brown liquid.  This material was highly acidic.(This is not true   when we checked it was actually basic)  The waster was removed to give a brown solid.~~

A number of analytical techniques, NMR (proton) in $D_2O$ and $CDCl_3$, IR and LC-MS, are in progress in an ~~to~~ attempt  at identification of the components of this material.

**<u>Comparison to Forward Drawn Sheet Study</u>**

The mentioned study [9] was an eighteen run designed experiment with line speed, corona treater power setting and corona treater gap as input variables. The samples were collected during the production of uniaxially machine direction oriented PET film.  AFM (~~surface topography and compositional variations~~s) were measured on the samples.  Surface roughness values, Ra, were determined for each sample.  Contact angle measurements were also taken immediately after production of the samples.

This study of corona treatment of uniaxially oriented sheet demonstrated that the watt-density employed during treatment as well as the corona gap setting have a direct impact on the surface roughness and the surface energy. During corona treatment low molecular weight species are generated by the energy imparted to the surface by the corona.   These materials are water soluble and upon removal the underlying pits and ~~ridges~~trenches induced by the corona are visible.

The high watt densities of the previous study showed extreme amounts of LMWOM on the surface as seen in Figure 8. This watt density is approximately 50% higher than in the PET film study. It is possible that the increased amount of LMWOM in the uniaxially drawn samples is related to the higher levels of amorphous ~~areas present~~areas present in those samples. This difference in crystallinity may provide more LMWOM than is observed in biaxially drawn PET film samples.

**Figure 8. 2x2 µm AFM image of a forward drawn sheet sample run at 63 ft/min line speed with a WD = 17.4 W/ft$^2$/min.**
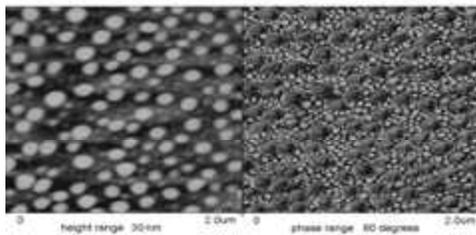


**ADHESION TO CORONA TREATED PET FILM (RE-DO THIS: ADD COMPARISON TO UNIAX STUDY…)**

Several questions arise concerning the mechanism of adhesion to corona treated film. How does one achieve adhesion with this LMWOM on the surface? Where does this material go when I process the film?

We can conclude that there is the creation of new functional groups on the surface during corona treatment and we see relatively small changes to the surface roughness. This means that the increase in wettability of the surface is due only to the production of these new functional groups and not to changes to surface roughness.

Chemically, when PET is corona treated, polymer chains are broken and the new functional groups appear. A significant number of these species are still attached to the film. These are the groups that give rise to the increased adhesion that is seen. This adhesion can be chemical and/or mechanical in nature.

It is less clear what role the LMWOM plays in the adhesion of materials to the surface of the PET film. In any event this material will participate in the bonding. This may explain why over-treatment of PET shows a loss of adhesion.

**CONCLUSION**

This study of corona treated biaxially oriented film samples of PET has demonstrated that the watt-density employed during treatment ha~~ve~~s a direct impact on the surface roughness and surface energy.~~.~~ During corona treatment low molecular weight materials are generated by the energy imparted to the surface by the corona. As in the previous study, ~~T~~these materials are water soluble and upon their removal the underlying pits and ridges ~~induced by the corona~~ are readily visible. This study of biaxially oriented film is consistent with the corona treatment of uniaxially oriented film.~~At higher watt-density treatment levels more pits and ridges are observed than at lower watt-density treatment levels.~~

The roughening induced by the corona~~at this point~~, as well as the LMWOM, may~~will~~ be carried through to any subsequent processing stages. The presence of water soluble materials on the film has implications for any process involving wettability and adhesion on PET films produced under corona treaters.

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