# Topographical and Chemical Characterization of Polymer Surfaces Modified by Physical and Chemical Processes

**Jeffrey A. Barish, Julie M. Goddard**

*Department of Food Science, University of Massachusetts, Amherst, Massachusetts*

Received 19 May 2010; accepted 1 September 2010
DOI 10.1002/app.33310
Published online 10 January 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Nanoscale changes to the surface of polymeric materials enables changes in materials' adhesion, wettability, printability, chemical functionality, and bioactivity, while maintaining desirable bulk properties. Polymer surface modification is therefore used in applications such as antimicrobial or non-fouling materials, biosensors, and active packaging. The range of available modification and analytical techniques used across laboratories prevents accurate comparison of techniques in terms of their effects on surface chemistry and topography. It was therefore our goal to evaluate the effects of four surface modification techniques (chromic acid, piranha solution, ultraviolet irradiation, and oxygen plasma) on polyethylene films. Changes in surface chemistry and topography were quantified using attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy, atomic force microscopy (AFM), contact angle measurement, and direct measurement of available surface carboxylic acids. Roughness increased in the order: piranha (57.7 nm); oxygen plasma (76.3 nm); UV irradiation (76.4 nm); chromic acid (120 nm). Hydrophobicity decreased in the order: piranha (77.20), chromic acid (73.50), oxygen plasma (61.70), UV irradiation (58.70). Functionalization (by IR absorbance intensity between 1680–1780 $cm^{-1}$) increased in the order: oxygen plasma (0.06), piranha (0.09), chromic acid (0.34), UV irradiation (0.50). By analyzing these methods using consistent analytical techniques, side-by-side comparisons have been accurately made. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2863–2871, 2011

**Key words:** polyethylene (PE); modification; surface modification; nanotechnology; functionalization of polymers

## INTRODUCTION

Polymer surface modification has widespread industrial importance in such varied applications as promoting adhesion, improving printability, modifying surface chemistry and topography, and reducing fouling of commercial polymeric materials.[1–5] Because changes in surface chemistry are often limited to the top several nanometers, surface modification can greatly alter how a polymer interacts with a biological environment, while maintaining the desirable bulk material properties. The biomedical field has a strong interest in the surface modification of polymers for the prevention of the biofouling of implanted devices, catheters, medical textiles, etc., in an on-going effort to reduce the instance of nosocomial infections.[6] Surface modification is also used to prevent nonspecific adsorption in bioanalytical assays and biosensors, thereby improving device sensitivity. It can also improve retained bioactivity of immobilized biomolecules and drug delivery systems.[7] In the food industry, polymer surface modification can enable development of unique active packaging applications in which active agents such as gas scavengers, flavor emitters/absorbers, time/temperature indicators, and antioxidants can be used to improve the quality of packaged foods.[8,9] Further, immobilization of antimicrobial agents onto surface-modified packaging films and processing surfaces can enable the design of safer food contact materials, which is critical as the need for improved food safety continues to grow.[10]

A number of techniques have been explored to impart surface chemistry modification of polymer films.[11–16] Physical techniques such as flame, corona discharge, ultraviolet (UV) radiation, plasma, gamma ray, electron beam, and laser treatments have the ability to modify the polymer surface through various chemical reactions.[11,15,17] Ideal surface modifications affect only the top nanometer of the polymer film's surface; however, very thin modifications are prone to surface reversal reactions, and thicker changes may affect bulk material properties.[15] Physical techniques offer advantages over wet chemical techniques by providing precise surface modifications without damaging the surface or the bulk properties of the film by overexposure.[1] Most physical techniques could be scaled up for large production without the associated chemical waste produced by wet chemical methods listed below.

Wet chemical techniques using chromic acid, potassium permanganate, or nitric acid are effective in surface modification by general oxidation reactions that

*Correspondence to:* J. M. Goddard (goddard@foodsci.umass.edu).

generate carbonyl, hydroxyl, and carboxylic acid groups.[18–20] These treatments are simple to perform in a wet chemical laboratory; however, results are often imprecise and can vary depending on the treatment conditions. In addition, wet chemical methods generate chemical waste, which limits interest in commercial uses.[21] Wet chemical methods are also susceptible to overexposure, which will damage the polymer surface and may result in undesirable bulk property changes. Nevertheless, such techniques are simple and rapid and can be carried out without the need for expensive specialized equipment, as many physical techniques require.

Despite the fact that each of these surface modification techniques has been previously reported, it is challenging to directly compare the effects of each technique on the topography and chemistry of polymer surfaces. Laboratory-to-laboratory differences in treatment and characterization methodologies prevent the ability for accurate side-by-side comparisons. It was, therefore, our goal to explore the chemical and topographical effects of UV irradiation, oxygen plasma, chromic acid oxidation, and piranha treatments on the surface modification of polyethylene.

### Objective

The objective of this research was to quantify and compare the molecular and topographical effects of common physical and chemical surface modification techniques on polyethylene films using techniques that are sensitive to nanoscale changes. The mechanistic differences between common techniques used in polymer surface modification were explored to directly compare the resulting changes in surface chemistry, wettability, and topography. Films were subjected to surface modification treatments for up to 15 min to evaluate the effect of treatment time on surface functionalization. Additional studies were conducted on UV-irradiated films to quantify the effect of UV treatments on the formation of low-molecular-weight water-soluble oligomers. Water contact angle, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), atomic force microscopy (AFM), and quantification of surface carboxylic acids were used to quantify nanoscale changes in surface chemistry and topography.

## MATERIALS AND METHODS

### Materials

Additive-free low-density polyethylene (LDPE, 125 mm) was donated by Honam Petrochemical (Seoul, South Korea). Toluidine blue O (TBO), hydrogen peroxide (30%), sulfuric acid, and anhydrous chromium trioxide were purchased from Fisher Scientific (Pittsburgh, PA). All other chemicals were of reagent grade or better and were used as received.

LDPE films were cut into 2 cm $\times$ 2 cm squares and were cleaned by sonicating for 10 min in two aliquots of isopropyl alcohol, then acetone, and then deionized (DI) water. Cleaned films were dried over anhydrous calcium sulfate and stored in clean glass Petri dishes.

### Surface functionalization

#### Chromic acid oxidation

Films were submerged for 5, 10, or 15 min in a 29 : 42 : 29 volumetric ratio of chromium trioxide to reagent grade DI water to concentrated sulfuric acid and treated at 70°C with slight shaking to ensure full coverage of the films.[22] Chromic acid-treated films were rinsed in copious DI water and then submerged in nitric acid maintained at 70°C for 15 min to dissolve any chromic salts that may have precipitated on the film surface during the treatment.

#### Piranha treatment

Piranha treatment is a commonly used cleaning process in which materials are exposed to a mixture of sulfuric acid and hydrogen peroxide to remove organic impurities. Film samples were submerged for 5, 10, or 15 min in a 5 : 1 volumetric ratio of concentrated sulfuric acid to hydrogen peroxide (30%) maintained at 70°C with slight shaking to ensure full coverage of the films (Piehler, 2000). Piranha-treated films were then rinsed in copious DI water.

#### UV irradiation

After a 5-min lamp warm-up period, films were irradiated for 5, 10, 15, 20, 25, or 30 min in a Jelight Co. model 42 UVO Cleaner (Irvine, CA), which emits 28 mW/cm$^2$ light at 254 nm at a distance of 2 cm. To quantify the formation of low-molecular weight water-soluble oligomers on film surfaces during UV treatment, surface analysis was conducted on films that had been irradiated for 10, 20, or 30 min with and without a post-treatment rinse in DI water.

#### Oxygen plasma

Films were treated with oxygen plasma for 5, 10, and 15 min in a Harrick Plasma Cleaner (Ithaca, NY) at 29.6 W and a vacuum pressure of 200 millitorr maintained by constant oxygen flow.

### Surface analysis

#### ATR-FTIR

Changes in surface chemistry were quantified using ATR-FTIR spectroscopy. ATR-FTIR spectra were collected on an IRPrestige 21 spectrometer (Shimadzu

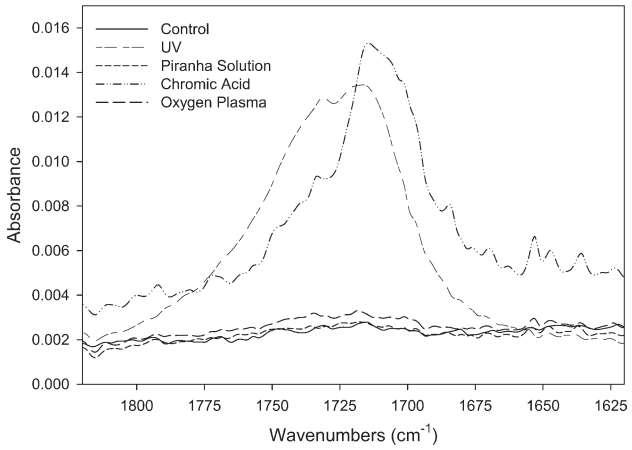


**Figure 1** ATR-FTIR spectra focusing on the range from 1660 to 1820 $cm^{-1}$. Spectra shown here are representative of nine replicate spectra collected from three independent film samples per treatment.

Corp., Tokyo, Japan) with a diamond ATR crystal. Each absorbance spectrum represents 32 scans at a 4 $cm^{-1}$ resolution using Happ–Genzel apodization, taken against a background spectrum of an empty ATR crystal. The resultant spectrum was collected using IRsolution software (Shimadzu Corp.) and analyzed using Knowitall software (Biorad Laboratories, Philadelphia, PA). Peak area was calculated after baseline correction using a five-point linear correction curve, and areas were averaged from nine scans (three repetitions on each of three independent film samples). Spectra illustrated in Figures 1 and 4 are representative of replicate spectra ($n = 9$) and have been smoothed by Fourier transform denoising by filtering using IRsolution software to facilitate comparison between techniques.

### AFM

AFM was used to quantify the effect of functionalization treatment on surface topography. Intermediate contact (tapping) mode images were taken on control and functionalized films on a Veeco CP-II (Veeco Corp., Santa Barbara, CA) using a Veeco cantilever tip with a force constant of 20 N/m and a resonant frequency of 267–319 kHz. For roughness calculations, the arithmetic average of absolute values ($R_a$) was calculated using ProScan Image Processing software, Version 2.1 (Veeco Corp.) from a three-dimensional roughness profile. Reported data were averaged from at least nine scans (three regions on three separate film samples).

### Contact angle

Water contact angles of control and surface-modified films were measured on a DSA100 (Kruss, Hamburg, Germany) to determine the effect of functionalization treatments on surface hydrophilicity. Pure Optima water was used as the probe liquid, and all measurements were conducted under standard atmospheric conditions. Advancing and receding contact angles ($n = 9$, three measurements on each of three separate films) were measured and calculated (average mean of three advancing and three receding measurements) using Drop Shape Analysis software, version 1.91.0.2 (Kruss).

### Quantification of surface carboxylic acids

The number of available carboxylic acids was quantified using TBO dye assay, which has been reported to complex with carboxylic acids in a modified equimolar ratio.[23,24] Briefly, control and surface-modified films ($n = 4$) were shaken for 2 h at room temperature in 0.5 m*M* TBO in DI water adjusted to pH 10 by NaOH, followed by rinsing in DI water adjusted to pH 10 by NaOH to remove noncomplexed dye. Complexed dye was desorbed by the immersion of films in 50 wt % acetic acid. Absorbance of the acetic acid solution was measured at 633 nm and compared with a standard response from a solution of 50 wt % dye in acetic acid. A slope equation was generated from the standard response and nmol/$cm^2$ was calculated using the absorbance value measured at 633 nm, the volume of acetic acid, and the surface area of the film.

### Statistical analysis

Statistical analysis was conducting using IBM SPSS statistics software (SPSS, Chicago, IL). Bivariate one-way analysis of variance tests were performed on each data set to determine statistical significance and standard deviations. Data sets were collected from at least nine regions (three regions on three different samples).

## RESULTS AND DISCUSSION

Control and surface-modified materials were analyzed by ATR-FTIR, AFM, contact angle, and dye assay to quantify the effect of each treatment, as well as treatment time, on surface topography and chemistry. It is important to note that although the authors acknowledge that interactions with liquid water impact the results from surface analyses, it was their goal to evaluate the chemical and topographical nature of material surfaces in their native state after treatment, despite the fact that some of the surface treatments (piranha and chromic acid) and some of the surface analytical techniques (contact angle and dye assay) inherently involve the interaction with liquid water.

### ATR-FTIR

Analysis of the ATR-FTIR spectra showed changes in surface chemistry in all the samples, suggesting the formation of carboxylic acids among other active

**TABLE I**
**ATR-FTIR Peak Area ($cm^{-1}$) Results Calculated from the 1680–1780 $cm^{-1}$ ranges**

| Treatment method | 5 min | 10 min | 15 min |
|---|---|---|---|
| Piranha solution | $0.04 \pm 0.02^{a,b}$ | $0.03 \pm 0.02^{b}$ | $0.09 \pm 0.01^{a}$ |
| Oxygen plasma | $0.07 \pm 0.03^{a,b}$ | $0.06 \pm 0.01^{a,b}$ | $0.06 \pm 0.02^{a,b}$ |
| UV-ozone | $0.17 \pm 0.02^{c}$ | $0.41 \pm 0.02^{d}$ | $0.50 \pm 0.01^{e}$ |
| Chromic acid | $0.38 \pm 0.02^{e}$ | $0.32 \pm 0.03^{f}$ | $0.34 \pm 0.04^{f}$ |

Values are means of $n = 9$ determinations $\pm$ standard deviations. Superscript letters indicate significant differences ($P < 0.05$) as determined by analysis of variance statistical analysis.

groups. Figure 1 displays representative spectra of samples treated for 15 min by each technique with an inset focusing on the 1660–1820 $cm^{-1}$ range where the most significant changes in absorbance were observed. To quantitatively compare the formation of reactive oxygen containing groups by the various treatments, peak area was calculated using Biorad Knowitall software to determine peak area between 1680 and 1780 $cm^{-1}$ range, which correspond to the absorbance band for carboxylic acids, in addition to other reactive functional groups. The peak areas of each technique at each time point were normalized by subtracting the average peak area determined for control (cleaned, untreated) samples, and are reported in Table I.

Piranha and oxygen plasma treatments resulted in only slight increases in absorbance in the 1680–1780 $cm^{-1}$ band versus control, and the length of treatment time had no significant effect. Both UV irradiation and chromic acid treatments resulted in significant increases in absorbance intensity after 5 min. UV irradiation treatment was the most time dependent, with increasing absorbance suggesting increasing formation of oxygenated reactive groups. Chromic acid treatment was the most effective for the formation of active groups on the surface of the film during short treatment times; however, active group formation reached a plateau after 5 min of treatment and was surpassed by UV treatment at the 10-min mark. Both UV irradiation and chromic acid treatments resulted in similar absorbance intensity in the region associated with the formation of carboxylic acids. It is interesting to note that for UV irradiation, the increase in peak area in the 1680–1780 $cm^{-1}$ band was caused by not only a change in peak height but also because of a widening of the absorbance band in the 1750-nm region, likely a result of the formation of additional active groups such as aldehydes (1740–1720 $cm^{-1}$), esters (1740–1715 $cm^{-1}$), or ketones (1745–1725 $cm^{-1}$).

## AFM

AFM imaging was conducted to determine the average surface roughness of the treated samples; this is an important parameter in the functionalization of polymer surfaces. Surface roughness may promote cell adhesion in biomedical materials[25] and can help to improve hydrophilicity, printability, and adhesion of composite structures such as laminates.[26] In many biological applications, however, surface roughness can lead to problems such as biofouling by providing small crevices for microbial growth or protein fouling.

The LDPE films used in this study had a moderate degree of native surface roughness because of extrusion of the film. It was observed that the extrusion lines from the production of the film had an average height of 230–250 nm, an average width of 40–50 nm, and repeated on the surface every 30–40 μm. To accurately quantify the effect of each treatment on surface roughness, roughness calculations were performed on 20 μm × 20 μm sections within the 50 μm × 50 μm micrograph to avoid macroscopic defects because of the extrusion process or physical damage, which were unrelated to roughness resulting from functionalization treatments. Figure 2 shows AFM images of samples treated for 15 min.

The surface roughness of each sample is listed in Table II. The control had an average surface roughness value of 54.62 nm of surface roughness, which

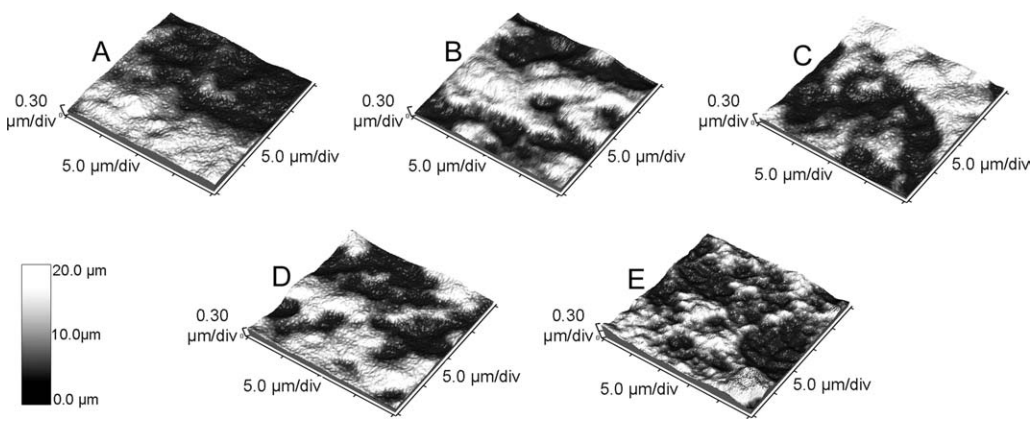


**Figure 2** AFM topography images for samples that have been treated for 15 min; (A) control, (B) piranha, (C) oxygen plasma, (D) UV, and (E) chromic acid.

**TABLE II**
**AFM Surface Roughness Measurements (nm)**

| Treatment method | 5 min | 10 min | 15 min |
|---|---|---|---|
| Control | 54.62 ± 4.13[a] | | |
| Piranha solution | 54.47 ± 2.39[a] | 55.39 ± 2.38[a] | 57.73 ± 2.18[a,b] |
| Oxygen plasma | 60.77 ± 1.39[b,c] | 68.83 ± 2.29[d] | 76.27 ± 1.23[e] |
| UV-ozone | 62.61 ± 1.81[c] | 72.56 ± 2.51[f] | 76.38 ± 1.64[e] |
| Chromic acid | 84.33 ± 2.20[g] | 92.02 ± 4.22[h] | 120.01 ± 4.00[i] |

Values are means of $n = 9$ determinations ± standard deviations. Superscript letters indicate significant differences ($P < 0.05$) as determined by analysis of variance statistical analysis.

represents a smooth and uniform surface. The piranha solution treatment resulted in insignificant differences in surface roughness regardless of the treatment time, supporting the ATR-FTIR spectral results, which indicated minimal functionalization by piranha treatment. Both the oxygen plasma and UV irradiation treatments showed significant increases in surface roughness with treatment time, with similar roughness values for each treatment at each time point. It is interesting that, for UV irradiation, the increase in roughness correlated to increasing surface functionality as determined by ATR-FTIR, but no such correlation was evident for oxygen plasma treatment. This may be because oxygen plasma is a surface-limited treatment, whereas UV irradiation may penetrate deeper into the film surface. Chromic acid treatment resulted in the greatest increase in surface roughness, with an average roughness of 84 nm at 5 min, increasing to 92 nm and 120 nm roughness after 10 and 15 min treatment, respectively. This increase in roughness with treatment time is in contrast to ATR-FTIR analysis, which suggested no increase in functionality with increasing chromic acid oxidation. Statistical analysis showed that the length of time for the chromic acid and UV irradiation treatments resulted in significantly different values.

## Contact angle

Contact angle measurement was performed to quantify the effect of each surface modification technique on surface hydrophobicity of the treated films. Contact angle measures the wettability of the surface, which could help with the adherence of water-soluble inks and coatings and may be an indicator for the likelihood of protein and microbial biofouling of a surface. The contact angle measurements for control and treated polyethylene films are shown in Table III where the values are averages of $n = 9$ measurements reported as both advancing and receding angles. The control sample presented a hydrophobic surface, typical of a clean polyethylene film. Each of the four different treatments resulted in increases in hydrophilicity; however, the results were varied and treatment time only had an effect in the case of oxygen plasma and UV irradiation treatments, most notably with UV irradiation.

The piranha treatment had the least effect on hydrophobicity compared with the control, although statistical analysis did show significant values, most notably after 15 min of treatment. Both the UV irradiation and oxygen plasma treatments had an increase in hydrophilicity at the 5-min mark, with incremental increases for both the 10- and 15-min treatments. Chromic acid-treated films had significant increases in hydrophilicity compared with the control, with a plateau effect resulting in insignificant changes despite the length of treatment time. It should be noted that formation of oxidized oligomers and volatile products will increase hydrophilicity as measured by contact angle; surface roughness can also cause similar effects.[27]

## Quantification of surface carboxylic acids

TBO dye assay confirmed the formation of available carboxylic acids on the surface of treated films. The

**TABLE III**
**Advancing ($\theta_A$) and Receding ($\theta_R$) Contact Angle Measurements (Degrees) for Each of the Different Modification Techniques**

| Treatment method | 5 min | 10 min | 15 min |
|---|---|---|---|
| Control | | $\theta_A$: 99.10 ± 1.33; $\theta_R$: 90.73 ± 0.65 | |
| Piranha solution | $\theta_A$: 82.85 ± 1.39 | $\theta_A$: 81.04 ± 2.48 | $\theta_A$: 76.75 ± 1.60 |
| | $\theta_R$: 70.31 ± 1.57 | $\theta_R$: 67.90 ± 1.46 | $\theta_R$: 64.38 ± 0.59 |
| Oxygen plasma | $\theta_A$: 70.83 ± 1.35 | $\theta_A$: 68.13 ± 1.52 | $\theta_A$: 65.03 ± 0.56 |
| | $\theta_R$: 59.72 ± 0.92 | $\theta_R$: 58.17 ± 0.84 | $\theta_R$: 52.94 ± 0.92 |
| UV-ozone | $\theta_A$: 74.20 ± 3.12 | $\theta_A$: 66.23 ± 1.61 | $\theta_A$: 66.52 ± 1.63 |
| | $\theta_R$: 61.79 ± 2.25 | $\theta_R$: 55.51 ± 3.11 | $\theta_R$: 52.87 ± 1.08 |
| Chromic acid | $\theta_A$: 71.35 ± 1.78 | $\theta_A$: 76.09 ± 0.63 | $\theta_A$: 75.74 ± 0.93 |
| | $\theta_R$: 58.84 ± 1.72 | $\theta_R$: 63.23 ± 0.83 | $\theta_R$: 61.78 ± 0.42 |

Values are means of $n = 9$ determinations ± standard deviations.

**TABLE IV**
**Quantification of Available Carboxylic Acids (nmol/cm$^2$)**

| Treatment technique | 5 min | 10 min | 15 min |
|---|---|---|---|
| Piranha solution | 0.06 ± 0.01[a] | 0.05 ± 0.01[a] | 0.07 ± 0.02[a] |
| Oxygen plasma | 0.09 ± 0.02[b] | 0.12 ± 0.01[b] | 0.12 ± 0.01[b] |
| UV-ozone | 0.03 ± 0.01[c] | 0.08 ± 0.01[a,b] | 0.10 ± 0.01[b] |
| Chromic acid | 1.43 ± 0.11[d] | 1.29 ± 0.12[e] | 1.48 ± 0.10[d] |

Values are means of $n = 9$ determinations ± standard deviations. Superscript letters indicate significant differences ($P < 0.05$) as determined by analysis of variance statistical analysis.

amount of available surface carboxylic acids (nmol/cm$^2$) generated by each technique at each time point were normalized by subtracting the average value determined using control (cleaned, untreated) samples, and are reported in Table IV. The piranha-treated samples generated minimal numbers of available surface carboxylic acids, with the length of treatment time having no significant effect, which is in support of the ATR-FTIR results, which indicate no significant increase in absorbance band around 1725 cm$^{-1}$. Oxygen plasma treatment resulted in formation of more available carboxylic acids than by piranha treatment, but with minimal effect by extending treatment time. UV irradiation generated a minor amount of available carboxylic acids at the 5-min mark, but significant increases were observed as the length of treatment time increased, eventually approaching the numbers of carboxylic acids achieved with oxygen plasma treatment. Chromic acid treatment generated the greatest number of available carboxylic acids, and treatment time had a minor effect. It is possible that the formation of significantly more available carboxylic acid groups by chromic acid oxidation versus the other techniques is a result of the higher degree of surface roughness, which increases the surface area over which the measured surface functionalization occurs.

The results from the TBO assay were not as expected compared with the ATR-FTIR results. The peak area measurements resulted in the observation that both the piranha and oxygen plasma treatments had similar values in addition to being much lower than both the UV and chromic acid treatments. In the case of available surface carboxylic acids, oxygen plasma treatment had significantly higher amounts than that of the piranha treatments. However, the most noteworthy results were observed during the UV treatments. ATR-FTIR spectra indicated that UV-treated samples had a significant amount of active group formation, approximately eight times the amount compared with the oxygen plasma treatments at the 15-min mark, in contrast to the number of available carboxylic acids determined by the TBO assay. This is likely a result of the generation of additional active groups on the surface of the polymer during the UV treatment, as noted by the widening of the absorbance band. It may also be because ATR-FTIR analyses probe nearly 1 μm into the surface, whereas the TBO dye assay only quantifies surface-available carboxylic acids. This supports the conclusion that surface functionality penetrates deeper in UV-irradiated samples, which may reduce the likelihood of hydrophobic recovery in UV-irradiated surfaces. It is also interesting that although the ATR-FTIR spectra indicated similar peak heights for both UV irradiation and chromic acid treatments, the amount of surface carboxylic acids was significantly different. In addition to the likelihood that UV irradiation results in the formation of additional active groups such as aldehydes, esters, and ketones, the high degree of roughness induced by chromic acid treatment likely increased the number of available surface carboxylic acids as quantified by the TBO dye assay.

## UV irradiation study

UV irradiation was shown to be a highly effective method for surface modification of polyethylene film, yielding an optimal combination of minimal roughness, high hydrophilicity, and formation of reactive oxygenated functional groups. Further experiments were performed to determine the optimal treatment time; 20-, 25-, 30-, and 60-min treatment times were tested in this study in addition to the 5-, 10-, and 15-min samples already discussed in this article. The 60-min sample was physically damaged by the heat generated during UV treatment and, therefore, was excluded from this study.

### ATR-FTIR

As previously observed, the absorbance band between 1680 and 1780 cm$^{-1}$ grew in intensity and

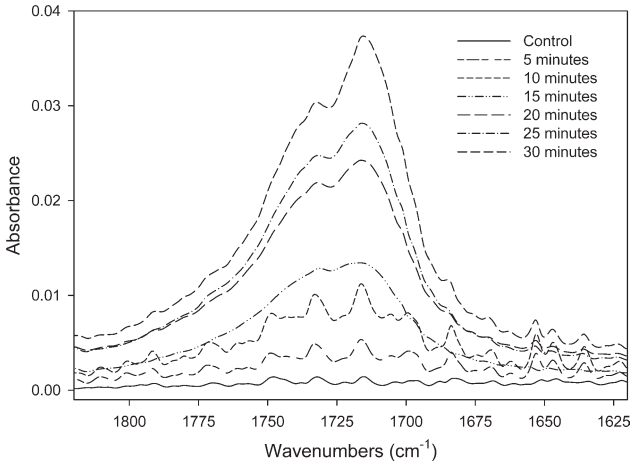


**Figure 3** ATR-FTIR spectra for control sample versus UV-treated films for determined time periods. Spectra shown here are representative spectra of control and UV-treated polyethylene films.

**TABLE V**
**Advancing ($\theta_A$) and Receding ($\theta_R$) Contact Angle Measurements (Degrees) Comparing Before and After Rinsing of UV-Treated Films. The Change in Contact Angle Is Also Reported**

| Treatment method | 5 min | 10 min | 15 min | 20 min | 25 min | 30 min |
|---|---|---|---|---|---|---|
| Before UV rinsing | $\theta_A$: 74.20 ± 3.13 | $\theta_A$: 66.24 ± 1.61 | $\theta_A$: 66.45 ± 1.63 | $\theta_A$: 69.45 ± 1.86 | $\theta_A$: 76.64 ± 1.30 | $\theta_A$: 72.19 ± 1.26 |
| | $\theta_R$: 61.79 ± 2.25 | $\theta_R$: 55.51 ± 3.11 | $\theta_R$: 52.87 ± 1.08 | $\theta_R$: 52.98 ± 0.75 | $\theta_R$: 55.46 ± 1.10 | $\theta_R$: 52.78 ± 1.16 |
| After UV rinsing | $\theta_A$: 78.51 ± 1.82 | $\theta_A$: 77.69 ± 2.15 | $\theta_A$: 81.28 ± 0.50 | $\theta_A$: 77.88 ± 0.30 | $\theta_A$: 87.16 ± 0.16 | $\theta_A$: 84.04 ± 2.39 |
| | $\theta_R$: 70.26 ± 1.36 | $\theta_R$: 59.64 ± 1.23 | $\theta_R$: 65.19 ± 2.01 | $\theta_R$: 56.63 ± 1.15 | $\theta_R$: 69.48 ± 0.78 | $\theta_R$: 77.26 ± 0.34 |
| Rinsing change | $\theta_A$: 4.31 | $\theta_A$: 11.45 | $\theta_A$: 14.83 | $\theta_A$: 8.43 | $\theta_A$: 10.52 | $\theta_A$: 11.85 |
| | $\theta_R$: 8.47 | $\theta_R$: 4.13 | $\theta_R$: 12.32 | $\theta_R$: 3.65 | $\theta_R$: 14.02 | $\theta_R$: 24.48 |

Values are means of $n = 9$ determinations ± standard deviations.

also widened with increasing treatment time, along with the associated increase in peak area (Fig. 3). Formation of a distinct second absorbance was observed in the 1740–1730 $cm^{-1}$ regions starting at the 20-min treatment, suggesting the presence of aldehydes, esters, or ketones. A large increase in absorbance occurred between the 15 and 20 min treatments, doubling absorbance intensity in the 1740–1720 $cm^{-1}$ region. However, small changes in band intensities were observed among the 20-, 25-, and 30-min samples even though the peak area significantly increased. Table V shows the average peak area results from the ATR-FTIR analysis, normalized by subtracting control absorbance within this band.

## AFM

As mentioned above, increasing surface roughness was observed between the 5-, 10-, and 15-min treatments. However, there was a marked decrease in surface roughness at the 20-min mark as seen in the shaded region of Figure 4, which may have been caused by the removal of oxidized oligomers by the cantilever tip during intermediate contact mode. The increase in surface roughness for the 25-min treatment may have been triggered by the penetration of UV light once the top 5 Å of material was oxidized from the UV treatment. The 30-min treatment also resulted in a relatively smooth surface, which is likely due to further generation of oxidized oligomers as observed after 20 min of treatment. This is an important concern when modifying the surface of polymer films; further tests are needed to determine whether any damage to the bulk properties of the film occurred because of the increased length of treatment time.

## Contact angle measurement

Increases in hydrophilicity were confirmed as treatment time increased up to 15 min. After this time, the surface regained hydrophobicity starting at the 20-min mark, reaching a plateau at the 25-min mark as observed in the shaded region of Figure 4. This may have been a result of disassociation of oxidized oligomers into the DI water used to measure the contact angle. Contact angle measurements for each time trial, before and after rinsing, shows that this trend is consistent throughout all the experiments, shown in Table V. Surface roughness of the polymer film may also affect the contact angle measurements, and a similar trend was observed in the AFM surface roughness results after 20 min of UV irradiation.

## Quantification of surface carboxylic acids

As the treatment time increased, an incremental increase in the number of available surface carboxylic acids occurred up to 15 min of treatment time. The largest increase in available carboxylic acids

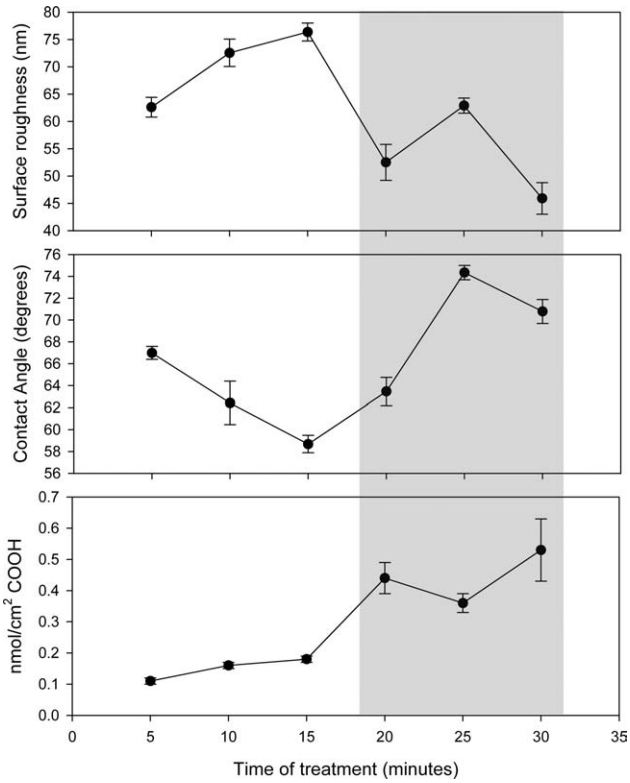


**Figure 4** Series of graphs comparing the control sample with the UV-treated samples for 5, 10, 15, 20, 25, or 30 min. Top, AFM surface roughness measurements; Middle, contact angle measurement; Bottom, available surface carboxylic acids from TBO assay. Shaded area highlights the trend described in the Results and Discussion section.

occurred between the 15- and 20-min treatment times where the number of available carboxylic acids more than doubled from 0.37 to 0.88 nmol/cm$^2$. A slight decrease occurred at the 25-min mark, likely because of the washing off of low-molecular-weight oxidized oligomers during the TBO assay, as observed by the other analytical techniques. The large standard deviations observed in the quantification of available carboxylic acids after 20 min treatment time is likely a result of irregular surface damage caused by extended UV irradiation treatment. Figure 4 shows the amount of available surface carboxylic acids formed by the UV irradiation treatment, also shading the area, which shows the similar trend seen in the results of the contact angle measurements and surface roughness.

In the extended UV irradiation study, it was consistently observed that trends in surface functionalization (whether hydrophilicity, roughness, or available carboxylic acids) changed around the 20-min mark as seen in the shaded region of Figure 4. One possible cause for this phenomenon could be from the excessive energy input during UV irradiation treatment resulting in polymer degradation and the generation of volatile products and oxidized oligomers.[27] ATR-FTIR analysis did not follow this trend primarily because the films were not rinsed between UV irradiation and ATR-FTIR analysis; therefore, the oxidized oligomers and volatile products never had the chance to disassociate from the surface before quantification was completed. Both the contact angle measurement and quantification of surface carboxylic acids involved the use of aqueous solutions that may have washed away some of the volatile products and oxidized oligomers from the surface, possibly resulting in this trend. AFM analysis also had this unusual trend occur, which may have been caused by the disassociation of the volatile products and oxidized oligomers from the intermediate contact of the cantilever as it touched the surface of the film.

## Rinsing study

Polymer surface functionalization primes surfaces for subsequent processes, including graft polymerizations, immobilization of bioactive compounds, or biopatterning. Because many of these subsequent processes occur in aqueous solution, and because results of the extended time UV irradiation study suggested the formation of water-soluble low-molecular-weight oxidized oligomers, it was of interest to understand the effect of rinsing on surface functionality of UV-irradiated films. In this study, films were treated by UV irradiation for 10, 20, or 30 min and then rinsed for 20 min (two baths of DI water for 10 min each). Contact angle measurements and ATR-FTIR spectra were collected to quantify the effect of rinsing in DI water on the functionality of UV-irradiated films.

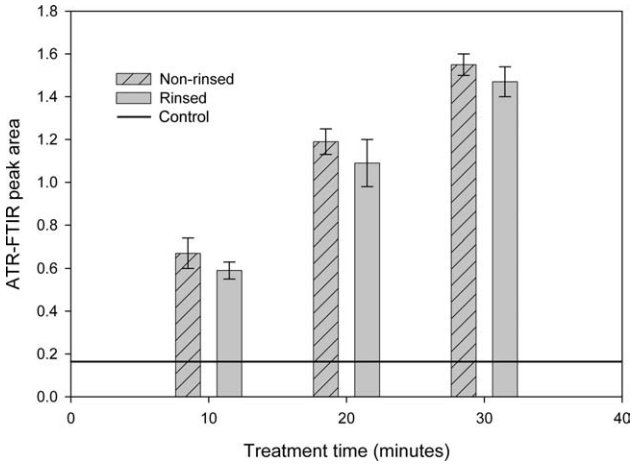


**Figure 5** ATR-FTIR peak area results for UV-irradiated polyethylene samples, which have either been rinsed in DI water or tested immediately after treatment without rinsing. The values are averages of peak area obtained from nine scans (three scans on each of the three samples).

### ATR-FTIR results

Absorbance intensity in the 1680–1780 cm$^{-1}$ region followed the same trend as previously noted (increased with treatment time); however, significant differences were observed compared with the rinsed samples. In each of the timed experiments, a decrease in the absorbance intensity was observed after the 20-min rinsing cycle. The oxygenated oligomers and volatile products formed during UV irradiation may be water soluble and can be rinsed off in DI water. Figure 5 compares the nonrinsed samples with the rinsed samples.

### Contact angle measurement results

Contact angle measurements confirmed the observations from ATR-FTIR analysis that water-soluble oxidized oligomers were rinsed from the surface of the modified films during the 20-min rinsing cycle. It is interesting to note that the hydrophobic recovery observed after the DI water rinse was uniform at about 20° regardless of contact angle or treatment time. These contact angles, although higher than the nonrinsed values, are still significantly lower than the control film contact angle, which confirms that polymer surfaces modified by UV irradiation retain functionality even after rinsing steps. This is an important consideration in applications where subsequent treatments are performed in aqueous solutions.

## CONCLUSIONS

In this work, we successfully tested four common surface modification methods for the functionalization of polyethylene film surfaces. Each method was capable of surface modification through surface chemistry and/or topographical changes to the outer

most layer of the film. Results concluded that some methods were more effective than others; however, it was also observed that certain methods imparted significant roughness to the polymer surface. The roughest surface was generated by chromic acid oxidation, which also resulted in the highest density of charged carboxylic acid groups as determined by TBO dye assay. The most hydrophilic surface was generated by 15 min treatment of either oxygen plasma or UV irradiation.

Overall, roughness increased in the order: piranha (57.7 nm); oxygen plasma (76.3 nm); UV irradiation (76.4 nm); and chromic acid (120 nm). Hydrophobicity decreased in the order: piranha (77.2°), chromic acid (73.5°), oxygen plasma (61.7°), and UV irradiation (58.7°). Functionalization (by IR absorbance intensity between 1680 and 1780 $cm^{-1}$) increased in the order: oxygen plasma (0.06), piranha (0.09), chromic acid (0.34), and UV irradiation (0.50). The best combination of minimal roughness, high hydrophilicity, and formation of reactive oxygenated functional groups was by UV irradiation. Comparison of ATR-FTIR, contact angle, and AFM results suggested that UV irradiation penetrates deeper into the film surface than oxygen plasma and wet chemical treatments, which may reduce the likelihood of hydrophobic recovery, thus improving the stability of surface functionalization treatments.

The least rough surface that presented moderate hydrophilicity resulted from piranha treatments; however, materials treated by piranha solution had low levels of functionalization as determined by dye assay and ATR-FTIR. To our knowledge, this is the first investigation of polymer surface modification by piranha treatment, which may be a promising alternative to chromic acid as a wet chemical treatment. It is likely that adjusting the ratio of hydrogen peroxide to sulfuric acid would result in a more aggressive piranha treatment, which may improve surface functionalization potential of piranha treatment.

On the basis of preliminary results of UV irradiation for polymer surface modification, further studies were conducted to observe the effects of longer treatment times and rinsing in DI water. The extended time study concluded that 20-min of treatment significantly increased the formation of available surface carboxylic acids. However, the surface roughness and contact angle measurements suggested that a certain degree of damage was caused to the surface of the film, which may be undesirable for further experiments. The rinsing study suggested that oxidized oligomers and volatile products may have been present on the polyethylene film after UV treatment, which were easily removed after 20 min of rinsing in DI water. This may result in complications when further film modification is the primary objective such as the grafting of monomer layers for bioactive compound attachment or the prevention of biofouling. By directly comparing these four methods in polymer surface modification using consistent surface analytical techniques, side-by-side comparisons have been accurately made. On-going work is investigating the use of these techniques as initial steps in the biofunctionalization of polymeric materials, for applications in the food and biomedical industries to improve safety and bioactivity.

The authors gratefully acknowledge Honam Petrochemical and Dr. Keun Taik Lee for the donation of LDPE film, and Jack Hirsch and Prof. Thomas J. McCarthy, Department of Polymer Science, for use of their oxygen plasma tool. They also thank Dr. D. Julian McClements for use of the Kruss DSA100 in addition to Jay Gilbert and Fang Tian for their help with data collection.

## References

1. Dasgupta, S. J Appl Polym Sci 1990, 41, 233.
2. Guruvenket, S.; Rao, G. M.; Komath, M.; Raichur, A. M. Appl Surf Sci 2004, 236, 278.
3. Hoffman, A. Macromol Symp 1996, 101, 443.
4. Ozdemir, M.; Yurteri, C. U.; Sadikoglu, H. Crit Rev Food Sci Nutr 1999, 39, 457.
5. Tao, G.; Gong, A.; Lu, J.; Sue, H. J.; Bergbreiter, D. E. Macromolecules 2001, 34, 7672.
6. Senaratne, W.; Andruzzi, L.; Ober, C. K. Biomacromolecules 2005, 6, 2427.
7. Goddard, J.; Hotchkiss, J. Prog Polym Sci 2007, 32, 698.
8. LaCoste, A.; Schaich, K. M.; Zumbrunnen, D.; Yam, K. L. Packag Technol Sci 2005, 18, 77.
9. Quintavalla, S.; Vicini, L. Meat Sci 2002, 62, 373.
10. Vermeiren, L.; Devlieghere, F.; Van Beest, M.; De Kruijf, N.; Debevere, J. Trends Food Sci Technol 1999, 10, 77.
11. Chan, C. M.; Ko, T. M.; Hiraoka, H. Surf Sci Rep 1996, 24, 1.
12. Deng, J.; Wang, L.; Liu, L.; Yang, W. Prog Polym Sci 2009, 34, 156.
13. Ikada, Y. Biomaterials 1994, 15, 725.
14. Liston, E.; Martinu, L.; Wertheimer, M. In Plasma Surface Modification of Polymers: Relevance to Adhesion; Strobel, M., Lyons, C. S., Mittal, K. L., Eds.; Vsp: Utrecht, The Netherlands, 1994; p 3.
15. Ratner, B. D. Biosens Bioelectron 1995, 10, 797.
16. Strobel, M.; Lyons, C.; Mittal, K. In Plasma Surface Modification of Polymers: Relevance to Adhesion; Strobel, M., Lyons, C. S., Mittal, K. L., Eds.; Vsp: Utrecht, The Netherlands, 1994.
17. Ozdemir, M.; Floros, J. Crit Rev Food Sci Nutr 2004, 44, 185.
18. Chatelier, R. C.; Xie, X.; Gengenbach, T. R.; Griesser, H. J. Langmuir 1995, 11, 2576.
19. Jansen, B.; Kohnen, W. J Ind Microbiol Biotechnol 1995, 15, 391.
20. Kong, J.; Chapline, M. G.; Dai, H. Appl Phys Lett 1995, 66, 159.
21. Penn, L.; Wang, H. Polym Adv Technol 1994, 5, 809.
22. Rasmussen, J. R.; Stedronsky, E. R.; Whitesides, G. M. J Am Chem Soc 1977, 99, 4736.
23. Kang, E.; Tan, K.; Kato, K.; Uyama, Y.; Ikada, Y. Macromolecules 1996, 29, 6872.
24. Uchida, E.; Uyama, Y.; Ikada, Y. Langmuir 1993, 9, 1121.
25. Faucheux, N.; Schweiss, R.; Lützow, K.; Werner, C.; Groth, T. Biomaterials 2004, 25, 2721.
26. Mathieson, I.; Bradley, R. Int J Adhes Adhes 1996, 16, 29.
27. Lee, K. T.; Goddard, J. M.; Hotchkiss, J. H. Packag Technol Sci 2008, 22, 139.