# Improved Surface Wettability of Polyurethane Films by Ultraviolet Ozone Treatment

**Ping Kuang,[1] Jae-Hwang Lee,[2] Chang-Hwang Kim,[2] Kai-Ming Ho,[2,3] Kristen Constant[1,3]**

[1]*Department of Materials Science and Engineering, Iowa State University of Science and Technology, Ames, Iowa 50011*
[2]*Department of Physics and Astronomy, Iowa State University of Science and Technology, Ames, Iowa 50011*
[3]*Ames Laboratory-U.S. D.O.E., Ames, Iowa 50011, USA*

Received 29 September 2009; accepted 26 April 2010
DOI 10.1002/app.32712

**ABSTRACT:** The wettability of polyurethane (PU) was altered using ultraviolet ozone (UVO) treatment. The effect of UVO treatment on PU surface chemistry was investigated with various experiments. The direct measurement of sessile drops was employed to quantify the static contact angle of different wetting liquids on homogeneous PU films with various UVO treatment times. The contact angle of DI water droplets was decreased to 17.2° from 70.04° after 5 min UVO treatment. The surface free energy of PU films was 51.46 mN $m^{-1}$ before treatment and was increased to 71.5 mN $m^{-1}$ after being fully treated. X-ray photoelectron spectroscopy (XPS) analysis shows a significant amount of polar functional species (C—O and C=O bonding) were formed on the PU surface by UVO treatment. atomic force microscopy (AFM) characterization shows the PU surface morphology was different before and after UVO treatment. The effect of water washing on UVO treated surface was also investigated. An aging effect study indicates the UVO modification can sustain the improved wettability with limited hydrophobic recovery, where the DI water contact angle remains constant at around 22° after the UVO treatment. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3024–3033, 2010

**Key words:** UVO treatment; polyurethanes; surface wettability; atomic force microscopy; X-ray photoelectron spectroscopy

## INTRODUCTION

Polyurethane (PU) is a versatile polymeric material that can exist in different solid forms, because of its wide range of molecular weights. PU rigid and flexible foams, adhesives, coatings, and molds are very common in both industry and research.[1,2] For coatings and molds specifically, they are elastomers and are typically produced by the reaction of organic isocyanates, high-molecular weight polyols, and low-molecular weight chain extenders.[3] Because these applications result in contact with various materials, PU surface properties can significantly influence their performance and a complete understanding and characterization of the surface properties, such as wettability of the PU, is needed. Furthermore, PU can be used for a wider range of applications if it possesses a surface that is modified and tailored.[4] For instance, PU is often used to fabricate patterned microstructures in various soft lithography techniques including microtransfer molding.[2] Modification of the surface is important to optimize the use of PU microstructures as molds in soft lithography, such as improved wetting for the infiltration of other materials. The purpose of this article is to investigate a simple and economical way to improve the surface wettability of PU molds for the infiltration of aqueous solutions such as ceramic slurries.

Different surface modification techniques such as multicomponent polyaddition reaction, oxygen plasma, and UV irradiation have been used to alter PU membranes or coatings to obtain a PU surface of better wettability.[3–5] One of the potentially more effective and economical methods for PU surface modification is ultraviolet ozone (UVO) treatment. In UVO treatment, two different UV radiations are present. One has a wavelength of 184.9 nm ($\lambda_1$), and the other has a wavelength of 253.7 nm ($\lambda_2$).[6] When the molecules on the surface of a thin PU film are exposed to the UV lights, excitation and dissociation of the polymeric molecules by the short-wavelength UV radiation take place. This is known as a photosensitized oxidation process.[7] Wettability of the film surface may be changed if the excited and dissociated PU molecules acquire different energies during the process. In addition, atomic oxygen is simultaneously generated when the oxygen molecules in air are dissociated by the

---

*Correspondence to:* K. Constant (constant@iastate.edu).
Contract grant sponsor: The Ames Laboratory, supported by the U.S. Department of Energy—Basic Energy Sciences; contract grant number: DE-AC02-07CH11358.

Journal of Applied Polymer Science, Vol. 118, 3024–3033 (2010)

184.9-nm UV light and the ozone molecules by the 253.7-nm UV light. When it is first produced by the dissociation of the oxygen molecules in air by the 184.9-nm UV radiation, the atomic oxygen will readily react with molecular oxygen to form ozone. Most hydrocarbons in PU and the ozone molecules can absorb the 253.7-nm UV radiation. Photolysis of ozone occurs and more highly reactive oxygen atoms are produced. Therefore, in UVO treatment when both wavelengths are present, oxygen atoms are continuously created and ozone is continuously created and destroyed. Most importantly, the highly reactive gaseous species, the atomic oxygen and ozone molecules, are oxidizing agents that may react with the surfaces of polymers to form peroxy and hydroxyl radicals, hydroperoxide, carbonyl, and carboxyl functionalities, which are responsible for the increased wettability of treated polymer surfaces.[5,8] The number of these radical functionality groups produced during the treatment are dependent on the ozone concentration and the exposure time as well as the treatment distance between the PU surface and the UV radiation source and water vapor concentration, etc.[6,8] While the surface may be greatly modified, the bulk of the PU films remain unchanged. The purpose of this study is to characterize the change of wettability of PU films under different UVO treatment times. It has been well-established that contact angle goniometry can be used to examine the wettability and measure the change in surface energy of a polymeric surface.[9] Static contact angle measurement was used to investigate the changes of the wettability in this study. The surface chemistry and morphology were studied using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) microscopy. The results of these investigations show that the UVO treatment significantly changes the surface properties of the PU films.

## EXPERIMENTAL

### Sample preparation

Lens Bond Optical Cement (J-91) from Edmund Optics (Barrington, NJ) was used as a PU source. PU films were prepared by spin coating the PU solution on Corning® cover glasses (No.2, 22 mm$^2$) at a spin speed of 4000 rpm for 1 min. Multiple spin-coatings were sometimes needed to produce smooth films. The PU films were immediately placed into a low-intensity UV curing machine (ELC-500 Light Exposure System, Electro-Lite Corporation) for at least 3 h for complete curing and solidification of the PU films. Scanning electron microscopy (SEM) images indicate that the thickness of the PU films is about 10 μm.

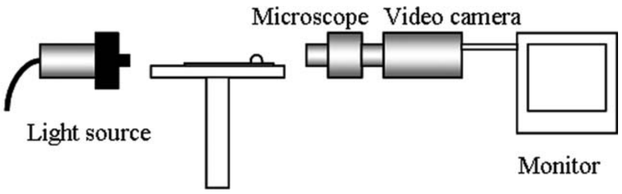

**Figure 1** Contact angle measuring system.

### UVO treatment

After the low-intensity UV curing, the PU films were placed in a UVO chamber (Model No.342, Jelight Company) at a distance 5mm below the UV light source for different treatment UVO treatment times to examine the effect on the surface of the PU films. The UV light source is a low-pressure mercury vapor grid lamp, and the output is 28,000 Micro Watts per cm in 254 nm frequency from 6mm distance. The interior of the chamber was kept at ambient conditions at the start of the treatment. For each treatment, the chamber was prerun for 5 min to achieve ozone gas and UV light saturation in the chamber. After the prerun, when the ozone gas content in the chamber remained at saturation level and the UV light power reached its saturation point, the PU films were immediately placed into the chamber for the UVO treatment. During treatment, an air pump remained running to maintain a steady ozone saturation level. After various UVO treatments, samples were taken out of the chamber and studies were carried out. The temperature of the UV chamber could rise to 67–70°C after the prerun and a maximum of 5 min UV exposure, because of heat from the UV lamp. AFM images show that the surface characteristics of PU films heated to 70°C on a hotplate are the same as the as-prepared PU films.

### Contact angle measurement

For the static sessile droplet contact angle measurement, PU films were placed on the sample stage of the contact angle measuring system, shown in Figure 1. A micropipette with disposable tips was used to place liquid droplets (∼ 1 μL) onto the surface of the films. Digital photos of the droplet profiles were taken within 10 s of the droplet placement with a video camera, which is attached to the optical microscope (×60). Multiple droplets were placed on the same PU film and measured under the same UVO conditions. A back LED diffuse light source provided illumination of the droplet profile. The microscope was tilted downward (∼ 2°) from the horizon so that the reflection of the droplet

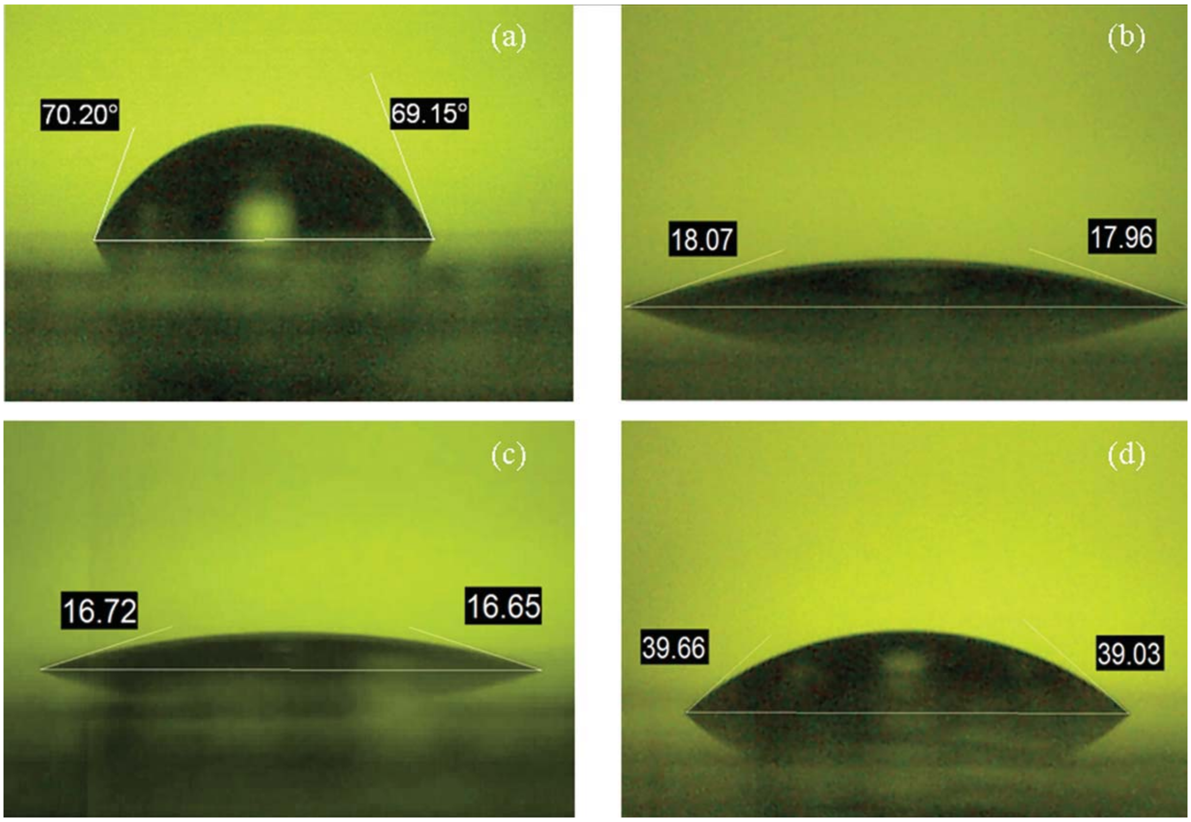

**Figure 2** Contact angle images of (a) DI water droplet on nontreated PU film, (b) DI water droplet on 600 s UV-ozone treated PU film, (c) CH2I2 droplet on nontreated PU film, and (d) CH2I2 droplet on 600 s UV-ozone treated PU film. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

profile was in view.[10] This was done to create a cusp at the air-liquid-solid phase intersection so the tangent to the droplet profile could be drawn to determine its contact angle on both sides (Fig. 2). Distilled water and Diiodomethane ($CH_2I_2$) (99%, Sigma-Aldrich, St. Louis, MO) liquid were used for the contact angle measurements. The contact angles of the liquid droplets in the digital photos were measured using the Quartz PCI software. Using the "angle measuring tool" in the software, the tangents to each side of the droplet were drawn and the value of the angles was calculated by the software.

### XPS and AFM

The XPS spectra were obtained with a PHI 5500 Multitechnique ESCA system (Perkin Elmer, East Cypress Street, Covina, California) by using the Al Kα (1486.6 eV) monochromatic X-ray source radiation. Pressure of the stainless steel sample analysis chamber was maintained at $1 \times 10^{-9}$ Pa. The binding energy (BE) scale was regulated by setting the C1s main peak at 285.0 eV. The resolution of the BE values was 0.2 eV. The data were examined by using the CasaXPS software for spectra deconvolution and curve-fitting. The surface morphologies of both untreated and 5 min UVO treated PU films were analyzed by AFM. The analysis was performed on a Multimode AFM microscope with a Nanoscope 3D ADCS controller (Veeco) in tapping mode with a silicon nitride cantilever.

## RESULTS AND DISCUSSION

### Contact angle analysis of PU films

Values of the average contact angles for two liquids, distilled water, and diiodomethane, on PU films with

**TABLE I**
**Average Values of Contact Angles (degrees) on PU Films with Different UVO Treatment Times**

| UVO time (s) | 0 | 10 | 20 | 40 | 60 | 80 | 100 | 300 | 600 |
|---|---|---|---|---|---|---|---|---|---|
| Liquid | | | | | | | | | |
| Distilled water | 71.04 | 49.21 | 48.61 | 43.40 | 33.76 | 25.23 | 16.84 | 17.17 | 17.64 |
| Diiodomethane | 17.20 | 46.80 | 48.95 | 48.34 | 46.64 | 43.30 | 41.61 | 40.06 | 39.95 |

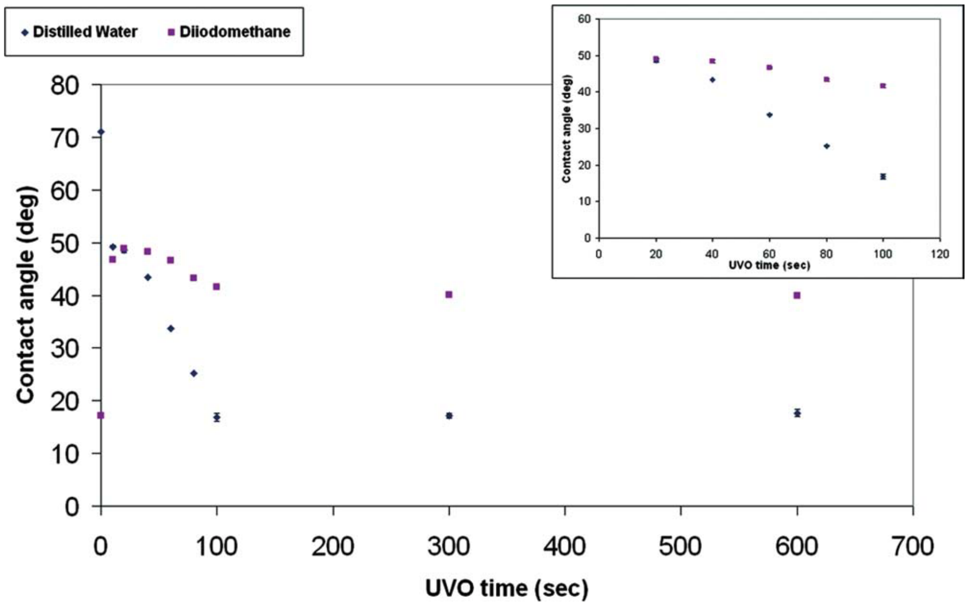

**Figure 3** Contact angles of distilled water and diiodomethane on PU films (Insert shows the middle regime when UVO time is between 20 and 100 s). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

various UVO treatment times, are shown in Table I. The UVO treatment times were chosen to be 0, 10, 20, 40, 60, 80, 100, 300, and 600 s. Each sample was only treated once for the given treatment time. At least three data sets (three droplets) were taken for each sample, which consisted of both left and right angles. The values of the contact angles are the averages of all data at each UVO treatment time taken in degrees. Hence, there were at least six contact angle values for each UVO treatment time. The contact angle of a distilled water droplet is 71.04° on the PU surface before any UVO treatment. Therefore, the PU surface is hydrophobic without surface modification and distilled water only partially wets the surface. The literature contact angle values of water on PU surface vary from 65° and 75°.[11,12] Therefore, the contact angle value of water on untreated PU films obtained in this experiment is within the predicted range. When the PU surface is UVO treated, its contact angle decreases. It was found that as the UVO treatment time was increased, up to a point, the contact angle of distilled water decreases continuously. Therefore, the PU surface becomes less hydrophobic and more hydrophilic. In contrast, before UVO treatment, the contact angle is 17.2° for the diiodomethane liquid. Hence, diiodomethane would wet the PU surface well without any surface modification. However, after UVO treatment, the contact angle for diiodomethane increases. The standard deviation of each data set was within 2° for distilled water and 1° for diiodomethane.

Figure 3 shows the trends of the contact angle for the two liquids. For both liquids, it is seen that even at very short UVO treatment time (10 s), the change of contact angles can be significant (~ 22° decrease for distilled water and ~ 30° increase for diiodomethane). This is because when PU films were first placed into the chamber, the surface of the films was exposed to the saturated ozone gas environment, and the ozone readily reacts with the PU surface and changes its surface chemistry immediately. For distilled water specifically, as the treatment time is increased to 20 s, the trend persists but at a greatly reduce rate. This indicates that the ozone effect on the PU surface takes place very quickly and reaches its maximum within 20 s. This also shows the ozone gas effect is not proportional to the ozone exposure time. When the UVO treatment times are between 20 s and 100 s (Fig. 3 Insert), the contact angles of distilled water droplets decrease gradually in an approximately linear fashion. This is contributed by the UV light, which can also alter the surface chemistry of the PU, because the dose of UV light in the chamber is linearly proportional to time. When UVO treatment is shorter than 20 s, the ozone effect dominates so this linear relationship is not seen from the plot. When the treatment times are between 20 s and 100 s, the UV effect is more evident, showing a linear trend. At UVO times greater than 100 s, the PU surface has been fully reacted with both ozone and UV light, and the contact angles remain constant at 17°. For diiodomethane at UVO treatment times shorter than 20 s when ozone effect dominates, the contact angles will increase with respect to treatment time and reach the maximum value of 48.95° at 20 s. This shows the ozone gas has the maximum effect on the PU surface at 20 s, and the ozone weakens

**TABLE II**
**Surface Tensions (in mN $m^{-1}$) of the Two Testing Liquids[14]**

| Liquid | $\gamma_{lv}$ | $\gamma_{lv}^{d}$ | $\gamma_{lv}^{h}$ |
|---|---|---|---|
| Water | 72.8 | 21.8 | 51.0 |
| Diiodomethane | 50.8 | 50.4 | 0.4 |

the wetting characteristics of diiodomethane on PU surface. However, for the 20–100 s regime, the contact angle results show a similar linearly decreasing trend as in distilled water as the treatment time increases, but the decreasing rate is lower than that of distilled water. This indicates that when the PU is treated by UV light, diiodomethane also becomes more wetting on the PU surface. At UVO times greater than 100 s, the PU surface is fully treated and the contact angles approach a constant value of 40°.

Therefore, it can be concluded that there are three stages in UVO treatment on PU surfaces where in the first stage the ozone effect dominates, in the second stage ozone effect diminishes and linear UV effect shows, and in the third stage the PU surface is fully treated.

## Surface free energy of PU films

The contact angle of a liquid drop, in equilibrium, on a solid surface is given by the well-known Young's equation:

$$\cos\ \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \tag{1}$$

where θ is the contact angle, $\gamma_{sv}$, $\gamma_{lv}$, and $\gamma_{sl}$ are the surface energy of solid against vapor, the surface energy of liquid against vapor, and the surface tension at the solid-liquid interface, respectively. From Young's equation, Owens and Wendt derived and proposed a general equation for calculating the surface free energy of solids, specifically, for low-surface energy materials such as polymers.[13] From the equation, the surface tension at the solid-liquid interface, $\gamma_{sl}$, is not required for the calculation.

$$1 + \cos\ \theta = 2\sqrt{\gamma_{lv}^{d}}\left(\frac{\sqrt{\gamma_{lv}^{d}}}{\gamma_{lv}}\right) + 2\sqrt{\gamma_{sv}^{h}}\left(\frac{\sqrt{\gamma_{lv}^{h}}}{\gamma_{lv}}\right) \tag{2}$$

where $\gamma_{lv}^{d}$, and $\gamma_{lv}^{h}$ are the dispersive component (nonpolar), hydrogen bonding (polar) component of the surface energy of a given liquid against vapor, respectively ($\gamma_{lv} = \gamma_{lv}^{d} + \gamma_{lv}^{h}$ ), and $\gamma_{sv}^{d}$, $\gamma_{sv}^{h}$ are the dispersive component and hydrogen component of the surface free energy of the solid against vapor. The dispersive component is contributed to by the dispersive van der Waals forces between the liquid and solid, and the hydrogen component includes nondispersive forces such as polar forces and hydrogen bonding forces. Additionally, $\gamma_{sv} = \gamma_{sv}^{d} + \gamma_{sv}^{h}$. As the component and the total surface free energy values are known for both liquids (Table II), and the contact angles for both liquids on PU films at different UVO treatment time was measured, it is possible to calculate the surface energy of the PU film at any given UVO treatment time. Figure 4 shows the plot for the dispersive component, the hydrogen component and the total surface energy values for PU films treated at different UVO times. The hydrogen component of surface energy is 5.36 mN $m^{-1}$ for PU surface and the dispersive component is 46.1 mN $m^{-1}$, therefore, the total surface free energy is 51.46 mN $m^{-1}$ when the PU film is not treated. The small hydrogen component value of PU indicates that there are only a few high-energy hydrogen bonds on the PU surface. Therefore, when it is in contact with a polar liquid such as water, the liquid does not wet the surface well. In contrast, because of the high-dispersive component value, diiodomethane (nonpolar) will wet the surface easily. It is shown that once the UVO treatment begins, the ozone effect in the beginning of the treatment leads to a significant increase in the hydrogen component values and significant decrease in the dispersive component values. Because of the highly reactive ozone gas, chain scission of PU polymer at the surface takes place very quickly and the long polymeric chains are broken. A significant number of high-energy polar ends of the broken chains are generated and exposed on the surface. This results in better wetting characteristics with distilled water and smaller contact angles

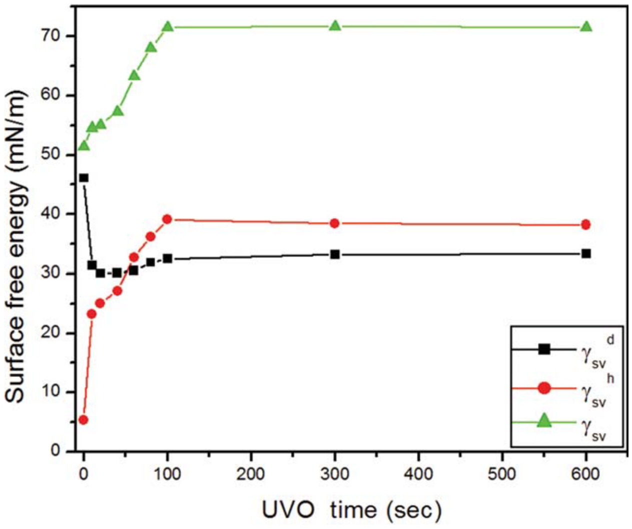

**Figure 4** Surface energies of PU solid films at different UVO times. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

result. In contrast, when the surface is in contact with diiodomethane, which is a nonpolar liquid, it becomes less wetting. As more high-energy polar ends are generated, the number of unbroken long chains on the PU surface decreases. Thus, the dispersive component of surface energy decreases. At the middle time regime (20–100 s) where the UV light effect is dominant, the linearly increasing trend of the hydrogen component (23.2–39.1 mN $m^{-1}$) corresponds to the linearly decreasing contact angle values for distilled water, and the linear increasing trend of the dispersive component (30.1–32.5 mN $m^{-1}$) corresponds to the linearly decreasing contact angle values for diiodomethane (Fig. 4). Increase in both components suggests that the UVO improves both van der Waals interactions and hydrogen bond interactions between the solid and liquid in the middle time regime. At longer UVO treatment time, each component approaches a constant value, which indicates that the PU surface has been fully treated by both ozone and UV light, and the free energy values for each component no longer increases. When the two components are added, the total value of the surface free energy increases linearly and reaches the constant value of 71.5 mN $m^{-1}$ after 100 s, when the PU surface is fully treated.

## Characterization of chemical surface changes

XPS analyzes were done for an untreated and a 5 min UVO treated PU films. The low-resolution scans of both films have the characteristic peaks corresponding to carbon (C 1s), oxygen (O 1s), and nitrogen (N1s) (scans not shown).[15] Furthermore, the scans show additional peaks corresponding to sulfur (S 1s), which is the specific composition of the PU prepolymer being used in this work. From the comparison of the low-resolution scans, it was noted that the oxygen level of the PU film was considerably increased after 5 min of UVO treatment.

For detailed chemical analysis, Figure 5(a,b) show the high-resolution spectra of the O 1s peaks for the untreated PU film and the 5 min UVO treated PU film. The C 1s spectrum of the untreated PU film can be deconvoluted into four subpeaks [Fig. 5(a)].[15] The peak at the lowest BE (285.0 eV) corresponds to (—C—C—) and (—C—H—) bonding. (Denoted **C1** in Fig. 1) The second peak (**C2**) is located at around 288.5 eV and corresponds to the (—N—CO—O—) group.[4] The peak at 286.3 eV (**C3**) corresponds to the (—C—O—C—) group, where carbon atoms are single-bonded to oxygen atoms. A very small peak (**C4**) can be located at 287.6 eV, which corresponds to urea groups (—N—CO—N—). The C 1s spectrum of PU film shows significant chemistry change after 5 min UVO treatment [Fig. 5(b)]. The peaks corresponding to oxygen-carbon double bonding (**C2, C4**) and single bonding (**C3**) are much higher in the treated sample than in the untreated sample. The significant increase of the oxygen content in each of the bonding species is attributed to the UVO treatment, which breaks the long molecular chains in the PU so oxygen can react and form oxygen-carbon single and double bonding groups. The surface energy of 5 min (300 s) UVO treated PU is already at its maximum, which is obtained at 100 s UVO treatment. This indicates that the PU surface is completely treated and the number of oxygen-carbon bonding groups is saturated. Therefore, the wetting angle measurements give the smallest value for DI water and the XPS studies show the maximum intensity of the peaks for various oxygen-carbon bonding species. The quantitative studies of the different species are shown in Table III.

The surface compositions, the integrated XPS intensity areas under each peak, of the untreated and treated PU films are listed in Table III. It can be seen that the area of **C1** is reduced from 68 to 51%, and the areas of **C2**, **C3**, and **C4** all have increased after 5 min UVO treatment. The ratio of the areas of carbon-oxygen single (C—O) and double (C[DBond]O) bonds to the area of the (—C—C—) bonding (**C1/C2** and **C1/C3**) are also calculated. The ratio of the integrated areas **C1/C2** and **C1/C3** were 3.66 and 5.39, respectively, when the PU film was untreated. This is because carbon-carbon bonding is the dominate species on the surface of the untreated PU. The ratio of the areas both were reduced to 1.71 and 2.98, respectively, for the 5 min UVO treated PU surface. The ratios of the C—C bond to the C—O and C=O bonds were reduced by about 50% after the treatment. The decrease in the area ratio after UVO treatment indicates the amount of the (—C—C—) bonding was decreased, while the C—O and C=O bonding increased. This observation suggests that the increased carbon-oxygen bonds, which are hydrophilic molecule groups, were the cause for the increased wettability of the PU films characterized by contact angle measurements.

## Changes in surface morphology

The 5 μm × 5 μm 3D AFM images in Figure 6(a,b) show the surface morphology of as-prepared, untreated and 5 min UVO treated PU films, respectively. The as-prepared PU samples are without any UVO treatment. The AFM 3D characterization shows that it has a smooth surface, with *z*-axis of 6 nm data scale. The area roughness analysis showed the $R_{rms}$ value was 0.392 nm. The 5 min UVO treated samples showed different surface morphology. The *z*-axis of the 3D image is 20 nm, which is much higher than the 3D image for the untreated sample. It shows many straight pillars with height around

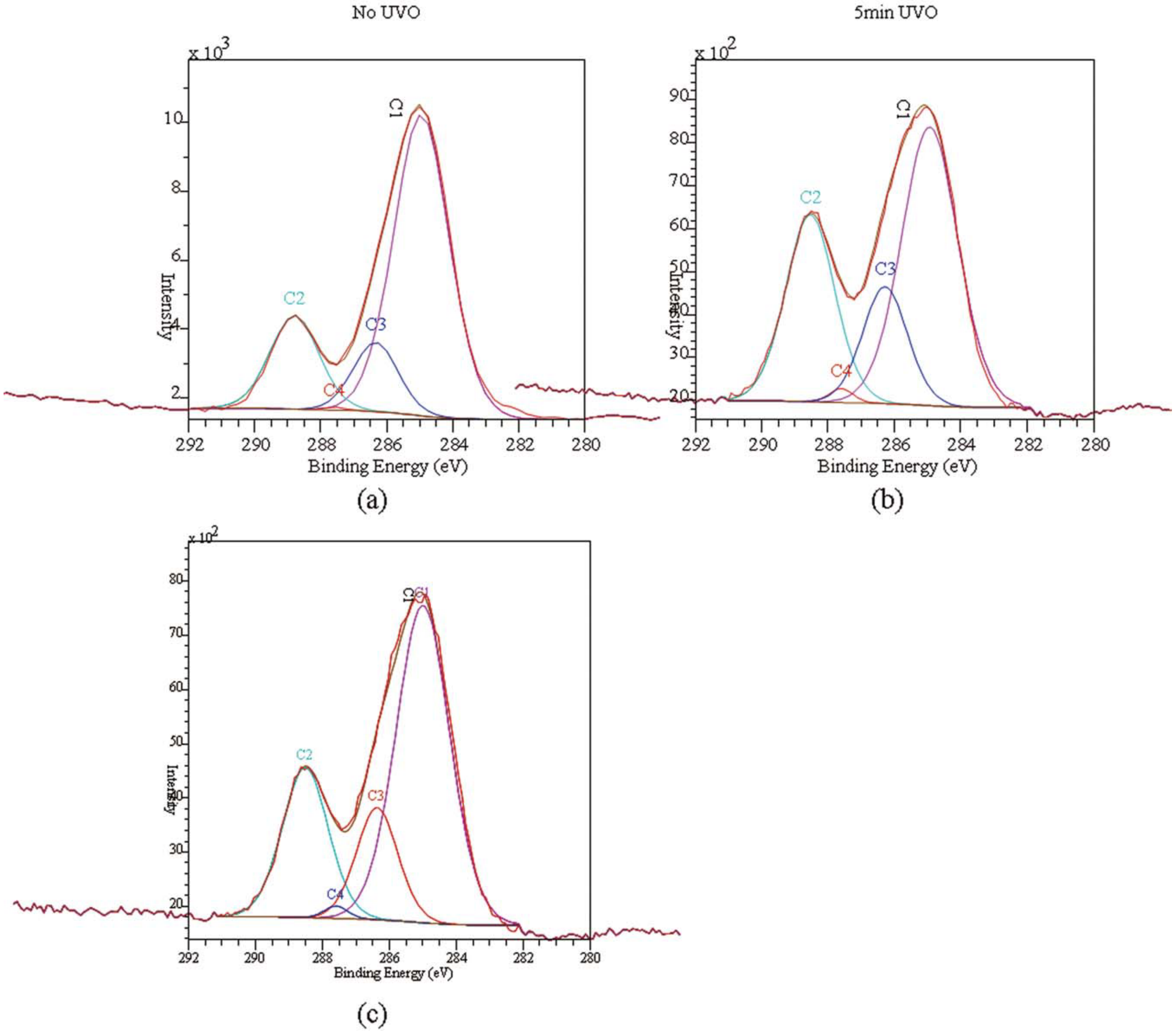

**Figure 5** High-resolution XPS spectra showing the deconvoluted C1s envelopes for (a) untreated PU film, (b) 5 min UVO treated PU film, and (c) 5 min UVO treated PU film after washing. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

3–8 nm. The $R_{\mathrm{rms}}$ values were also increased to 2.073 nm for the area roughness analysis. The pillars are low-molecular weight oxidized species, which were created when the PU surface was treated by UVO. The AFM images above were taken round 1 h after 5 min UVO treatment on the PU film surface without contacting any water, therefore, the low-molecular weight oxidized species could be observed. It is intuitive to state, from previous studies of different short UVO treatment times (Table I), as the UVO treatment time increases (10–100 s), more and more low-molecular weight oxidized species were created on the surface, thus the contact angle of water on treated PU surface gradually decreases (from 49–17°). As the treatment time is longer than 100 s, the low-molecular weight oxidized species are saturated on the PU film surface, and the water contact angle is stabilized at

**TABLE III**
**Surface Composition (Area %) of Untreated and 5 min UVO Treated PU Thin Films**

| Peak area (%) | C1 | C2 | C3 | C4 | C1/C2 | C1/C3 |
|---|---|---|---|---|---|---|
| Untreated | 68.35 | 18.69 | 12.68 | 0.28 | **3.66** | **5.39** |
| UVO treated | 51.46 | 30.15 | 17.29 | 1.10 | **1.71** | **2.98** |
| UVO treated DI water washed | 58.92 | 23.92 | 16.11 | 1.05 | **2.46** | **3.66** |

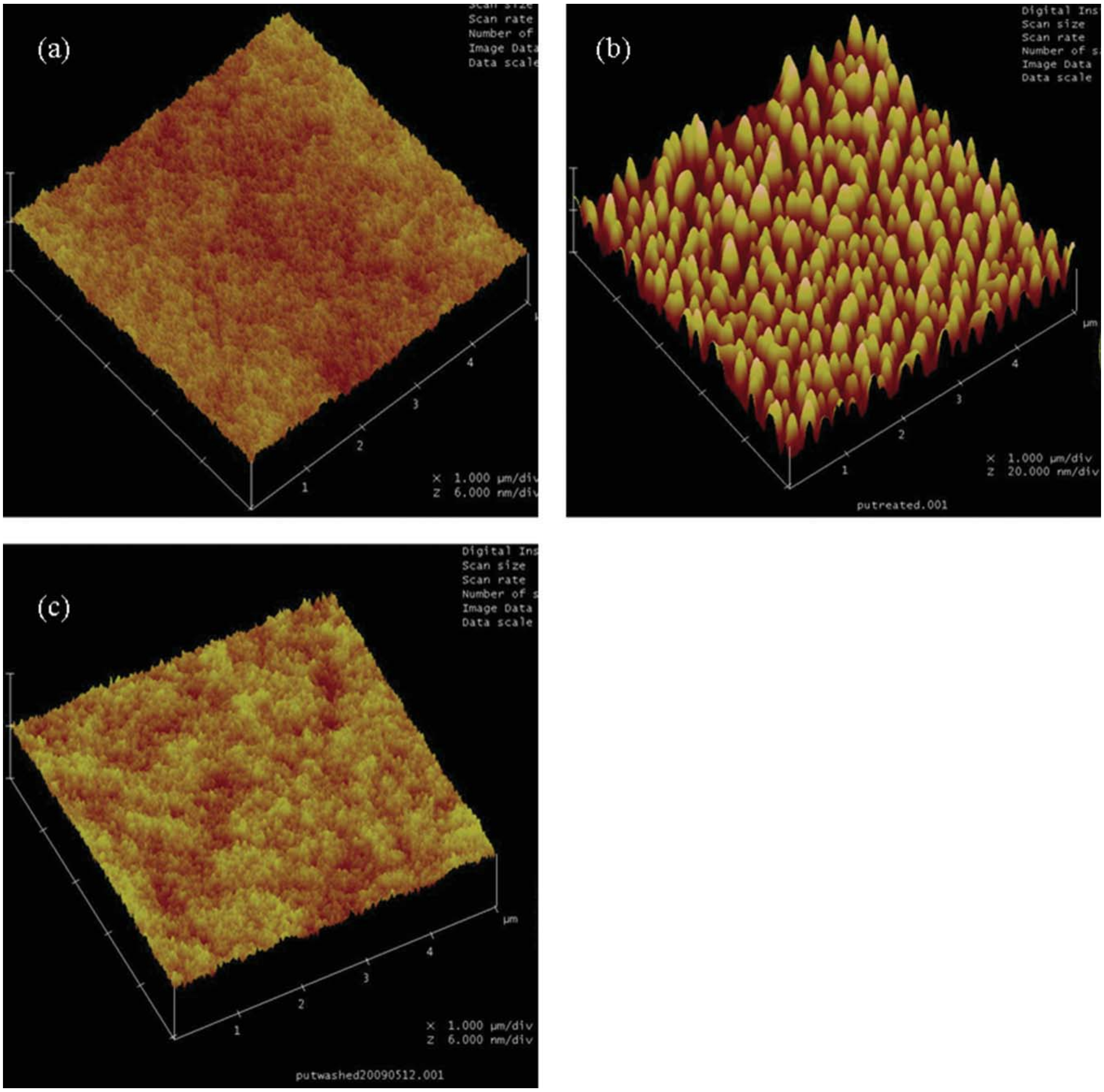

**Figure 6** The 5 µm × 5 µm 3D AFM images of (a) untreated PU thin film with rms roughness $w = 0.392$ nm, (b) PU thin film treated by 5 min UVO with $w = 2.073$ nm, and (c) 5 min UVO treated PU thin film after washing with $w = 0.321$ nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

around 17°. We can also relate these low-molecular weight oxidized species to the XPS results, where for the 5 min UVO treated samples, the oxygen-containing species content are significantly increased. It is reasonable to state that the oxygen groups (**C2**, **C3**, and **C4**) are created by the UVO where chain scission takes place and oxygen-containing free radicals are formed, and they are observed as straight pillars in the AFM image.

Unlike oxygen plasma etching,[15] the UVO treatment does not physically remove material from the surface. Instead, UVO treatment only breaks the long chain (—C—C—) bonds at the very surface of the PU film and inserts atomic oxygen and ozone molecules at the chain ends to create C—O and C=O bonding resulting in a much more hydrophilic surface. This nondestructive surface wettability functionalization proves to be advantageous as compared to the oxygen plasma etching method.

### Effect of water washing

The UVO treated PU thin films were also studied after washing with DI water. The effect of water washing on UVO treated polymer surfaces has already been characterized for some treated polymer surfaces.[16] For the PU film surface in this study, a 5 min UVO treated PU film was placed in a DI water bath and ultrasonicated for 5 min immediately after the UVO treatment. Then the sample was dried with blowing air and XPS and AFM studies were done within an hour. The XPS spectrum [Fig. 5(c)] of the treated and washed sample has the same characteristic peaks as the untreated and 5 min UVO treated samples. The intensity of the peaks corresponding to oxygen-containing species (**C2**, **C3**) is noticeably reduced comparing to the 5 min UVO treated sample [Fig. 5(b)]. However, the intensity of those peaks is still higher than the untreated PU surface [Fig. 5(a)]. The surface compositional study (Table III) also quantitatively shows the **C1** area is increased from 51% for 5 min UVO treated to almost 59% after washing of the treated sample. The ratio of the integrated areas **C1/C2** and **C1/C3** were 2.46 and 3.66, respectively. This indicates that some of the low-molecular weight oxygen-containing species created on the PU surface by UVO treatment was removed by water washing. Nevertheless, the water washed sample shows more oxygen content than the untreated sample which was sustained even after the washing. The 3D AFM image of the treated and washed sample is shown in Figure 6(c). It shows a little difference in morphology from the untreated sample, and the $R_{\mathrm{ms}}$ values were 0.321 nm for the area roughness analysis, which is also comparable with the untreated sample. The low-molecular weight oxidized species must have been dissolved and removed during the washing and a flat and smooth surface was observed by the AFM studies. This confirms with the XPS results that the oxygen content levels of the washed sample were lower than UVO treated sample. Static water contact angle measurements for the washed samples were also taken, and it is about 48°, which is higher than the water contact angle of the 5 min UVO treated sample (17°, Table I) but still lower than the untreated PU films (70°).

## Hydrophobic recovery

It is important to investigate the surface modification effect of UVO treatment on the PU surface over time to examine the hydrophobic recovery. The static contact angle measurement of DI water droplets on 5 min UVO treated PU films were done at different aging times (Fig. 7). The DI water contact angle on a one-day-old PU film was 17.2°, which was nearly the same as the contact angle measured right after the UVO treatment (dotted line, Fig. 7). The contact angle was increased to around 19.8° after two days of aging and reached a constant value of about 21–22° after 3 days. However, this small hydrophobic recovery is negligible when compared with the hydrophobic nature of the untreated PU films (dashed line, Fig. 7). This suggests that most hydrophilic single and double carbon-oxygen bond species remained on the PU surface permanently after being modified by UVO and the modification can sustain the improved wettability with limited hydrophobic recovery. It was also noted that after the UVO treatment, the transparent PU surface changed to yellowish color. This yellowish color disappeared after the hydrophobic recovery measurements were completed. It is caused by the high UV dose on the PU surface during the treatment. However, no further study was done to investigate the yellowing effect of the UVO on PU surface.

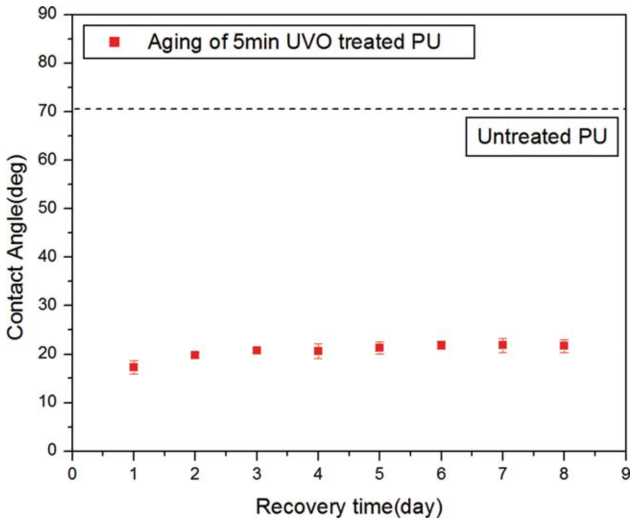

**Figure 7** Change of the water static contact angle values versus aging time for PU thin films after 5 min of UVO exposure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

## Treatment effects of UV/ozone on PU

Nanomechanical characterization of PU films for both as-deposited and UVO treated was carried out to determine the effect of treatment on mechanical properties. Results of nanoindentation (Micro Materials, NanoTest$^{\mathrm{TM}}$) suggest that UVO treatment results in a modest increase in hardness as measured by the slope upon unloading of the load-displacement curve. The ratio of hardness of treated to untreated films varies from 1.7 to 2. Studies with varying maximum load, loading rate, and dwell time at maximum load suggest that the mechanical properties are graded within the affected depth of about 1.0 μm. Creep at maximum load decreased slightly for treated films as compared to untreated films suggesting that viscoelasticity is reduced by UVO treatment. Because the total film thickness is about 10 μm, it can be concluded that the UVO treatment is confined to the PU surface.

## CONCLUSION

In this study, it was shown that the wetting properties of a PU film can be significantly changed by modifying the surface with UVO treatment. The two liquids tested showed different wetting phenomena. The ozone has an immediate impact on the PU surface and changes the wetting properties of PU surface significantly in the beginning stage of the UVO treatment. At the middle time regime, the UVO effect on PU surface is proportional to time until the PU surface has been fully treated. The UVO effect improves both polar and nonpolar interactions between the liquids and the PU surface at the middle time regime. The total surface free energy of the PU films increases in a linear fashion until the PU surface is fully treated. The total surface tension free energy of a fully treated PU surface is 71.5 mN $m^{-1}$. XPS analysis shows noticeable amount of hydrophilic C—O and C═O bonding species were created on the PU surface by UVO treatment. This results in the higher surface tension, free energy, and improved surface wettability. AFM images show different surface morphologies created by the UVO treatment. The effect of water washing on the UVO treated PU surface was also characterized, and it was revealed by AFM that some of the low-molecular weight oxidized species created by UVO treatment are removed, but the oxygen content is still high after washing when compared with untreated samples. The nondestructive surface modification proves advantageous compared with oxygen plasma etching methods.

Additional experiments with distilled water were also conducted for one-layer PU grating molds (2.5 μm pitch) made by the microtransfer molding (μTM) technique.[2] It was shown that on the structured non-treated one-layer PU mold, superhydrophobicity occurred and the contact angle of a water droplet was about 140°. When sufficient UVO treatment was done on the mold, the water droplet collapsed and was pulled into the channels because of the improvement on the wetting characteristics of the PU mold. This opens up a door for future studies on the infiltration of aqueous slurry into 3D polymeric structures at microsize,[2] and such studies will contribute to making microsize ceramic photonic band gap crystals in a more economical way.[17]

The authors would like to thank J. Anderegg for the assistance on XPS analysis, Gaurav Mohanty on nanoindentation testing analysis, and K.S. Nalwa on AFM analysis, and for meaningful discussions with Professor Zhiqun Lin.
This work is supported by the Director for Energy Research, Office of Basic Energy Sciences. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358.

### References

1. Randall, D.; Lee, S. The polyurethanes book; Wiley: New York, 2002.
2. Lee, J. H.; Kim, C. H.; Ho, K. M.; Constant, K. Adv Mat 2005, 17, 2481.
3. Ozdemir, Y.; Hasirci, N.; Serbetci, K. J Mater Sci Mater Med 2002, 13, 1147.
4. Muller, J. P.; Mitzner, E.; Goering, H.; Gahde, J. J Mater Sci Lett 1997, 17, 115.
5. Singh, R. P.; Tome, N. S.; Bhadraiah, S. V. Polym Degrad Stab 2001, 73, 443.
6. Macmanus, L. F.; Walzak, M. J.; Mcintyre, N. S. J Polym Sci Part A: Polym Chem 1999, 37, 2489.
7. Efimenko, K.; Wallace, W. E.; Genzer, J. J Colloid Interface Sci 2002, 254, 306.
8. Romero-Sanchez, M. D.; Pastor-Blas, M. M.; Martin-Martinez, J. M.; Walzak, M. J. Int J Adhes Adhes 2005, 25, 358.
9. Mcintyre, N. S.; Walzak, M. J. Mod Plast 1995, 72, 83.
10. Kwok, D. Y.; Neumann, A. W. In Contact Angle Techniques and Measurements, Surface Characterization Methods: Principles, Techniques, and Applications, Milling, A. J., Ed. Marcel Dekker: New York, 1999; p 49.
11. Sidouni, F. Z.; Nurdin, N.; Chabrecek, P.; Lohmann, D.; Vogt, J.; Xanthopoulos, N.; Mathieu, H. J.; Francois, P.; Vaudaux, P.; Descouts, P. Surf Sci 2001, 491, 355.
12. Chen, X.; You, B.; Zhou, S.; Wu, L. Surf Interface Anal 2003, 35, 369.
13. Owens, D. K.; Wendt, R. J Appl Polym Sci 1969, 13, 1741.
14. Butt, H.; Raiteri, R. In Surface Tension and Surface Stress of Solids, Surface Characterization Methods: Principles, Techniques, and Applications, Milling, A. J., Ed.; Marcel Dekker: New York, 1999; p 23.
15. Sanchis, M. R.; Calvo, O.; Fenollar, O.; Garcia, D.; Balart, R. J Appl Polym Sci 2007, 105, 1077.
16. Teare, D. O. H.; Ton-That, C.; Bradley, R. H. Surf Interface Anal 2000, 29, 276.
17. Lee, J.-H.; Kuang, P.; Leung, W.; Kim, Y.-S.; Park, J.-M.; Kang, H.; Constant, K.; Ho, K.-M. Appl Phys Lett 2010, 96, 193303.