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Increased Wettability and Surface Free Energy of Polyurethane by Ultraviolet Ozone Treatment

Ping Kuang and Kristen Constant

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 UV ozone treatment times. The contact angle of DI water droplets was decreased to 17.2º from 70.04º after 5min UVO treatment. The surface free energy of PU films was 51.46mN/m prior to treatment and was increased to 71.5mN/m after being fully treated. X-ray Photoelectron Spectroscopy (XP) 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 UV ozone modification can sustain the improved wettability with limited hydrophobic recovery, where the DI water contact angle remains constant at around 22º after the UVO treatment.

Keywords: UV ozone treatment, Surface energy, Contact angles, Surface wettability

1. Introduction

Polyurethane (PU) is a versatile polymeric material which, due to its wide range of molecular weights, can exist in different solid forms. In industry, PU is commonly used as rigid and

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flexible foams, adhesives, coatings, and molds [1-2]. PU coatings and molds are formed by the reaction of organic isocyanates, high molecular weight polyols, and low molecular weight chain extenders, and they are usually elastomers [3]. Because elastomeric PU is frequently used in contact with various materials, optimizing the PU surface properties is critical for enhancing their performance. Furthermore, complete understanding and characterization of PU surface properties, such as its wettability, is helpful for various practical applications. Moreover, a wide range of novel applications can be realized if the PU surface properties can be modified and tailored [4].

One novel application of PU is for fabricating patterned microstructures using microtransfer molding, which is one of various soft lithography techniques [2]. It was shown that, when using PU microstructures as molds in soft lithography, modification of the surface is important to achieve improved wetting for the infiltration of slurries or sol-gel materials. The purpose of this work was to utilize a simple and economical way to improve the surface wettability of PU molds for the infiltration of aqueous solutions including slurries of oxide nanoparticles.

Surface treatments are frequently used to modify the surface chemistry and improve wetting characteristics of polymers prior to use in a range of technological applications. Such treatments are necessary because the intrinsic activities of the polymer surfaces are frequently too low to allow satisfactory adhesion of surface coatings or laminates. Oxidation processes in the gaseous phase introduce a range of functionalities at the polymer surface therefore increasing the polar component of free energy. Gas phase treatments require the impingement of reactive species, such as oxygen radicals, on the polymer surface. In order to alter PU membranes or coatings to obtain a PU surface with better wettability, different surface modification techniques such as multicomponent poly-addition reactions, oxygen plasma, and ultraviolet (UV) irradiation have been used [3-5].

Another simple yet effective method for polyurethane surface modification is UV ozone (UVO) treatment. UVO treatment has been used to modify the surface wettability of various polymers [6-13]. A summary of selected previous work appears in Table 1. However, no experimental work had been done on polyurethane before our work.

Here, we show that UVO can have a much more significant impact on polyurethane surface. In UVO treatment for polymer surface modification, there are two different wavelengths of UV radiation present, 184.9 nm (λ_1) and 253.7 nm (λ_2) [14]. When the molecules on the surface of, as an example, a thin PU film are exposed to UV light, the shorter-wavelength UV radiation (λ_1) will induce excitation and dissociation of the polymeric molecules. This is known as a photo-sensitized oxidation process [11]. Wettability of the film surface may be changed if the excited and dissociated PU molecules acquire different surface energies during this process. In addition, atomic oxygen is simultaneously generated when the oxygen molecules in air are dissociated by the 184.9 nm UV light and the ozone molecules by the 253.7 nm UV light. Upon 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 wave-

Year	Paper	Materials
1996	"Improved adhesion to polymers by UV/ozone surface oxidation", Mathieson and Bradley, Int. J. Adhes. Adhes. [6]	Polyethylene (PE), polyetheretherketone (PEEK)
1998	"Surface modification of polyolefine by UV light/ozone treatment", Hu et al., J. Appl. Polym. Sci. [7]	Polyethylene (PE), polypropylene (PP)
1999	"Surface characterisation of ultraviolet-ozone treated PET using atomic force microscopy and X-ray photoelectron spectroscopy", Ton-That, C. et al., Surf. Sci. [8]	Polyethylene terephthalate (PET)
1999	"Atomic force microscopy study of polypropylene surfaces treated by UV and ozone exposure: modification of morphology and adhesion force", Nie et al., Appl. Surf. Sci. [9]	Polypropylene (PP)
2000	"Surface characterization and ageing of ultraviolet–ozone-treated polymers using atomic force microscopy and x-ray photoelectron spectroscopy", Bradley et al., Surf. Interface Anal. [10]	Poly(ethylene terephthalate) (PET), polystyrene (PS)
2002	"Surface Modification of Sylgard-184 Poly(dimethyl siloxane) Networks by Ultraviolet and Ultraviolet Ozone Treatment", Genzer et al., J. Coll. & Int. Sci. [11]	Poly(dimethyl siloxane) (PDMS)
2005	"Addition of ozone in the UV radiation treatment of a synthetic styrene-butadiene-styrene (SBS) rubber", Martin-Martinez et al., J. Adh. & Adh. [12]	Styrene-butadiene-styrene (SBS) rubber
2008	"Surface modification of poly (lactic acid) by UV/Ozone irradiation", Koo and Jang, Fiber Polym. [13]	Poly(lactic acid) (PLA)

Table 1. List of previous work of UVO treatment on various polymers

lengths 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 polymer surfaces to form peroxy and hydroxyl radicals, hydro-peroxide, carbonyl, and carboxyl functionalities, which are responsible for the increased wettability of treated polymer surfaces [5, 12]. The number of these radical functionality groups produced during the treatment is dependent on the ozone concentration and exposure time, the presence of water vapor, and the distance between the PU surface and the UV radiation source, among other factors [12, 14]. 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 [15]. 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). The results of these investigations show that the UVO treatment significantly changes the surface properties of the PU films.

1.1. Wettability study of PU films by contact angle measurements

For static sessile droplet contact angle measurement, PU films were placed on the sample stage of the contact angle measuring system, shown in Figure 1. Distilled water and diiodomethane (CH_2I_2) (99%, Sigma-Aldrich) liquid were used for the contact angle measurements.
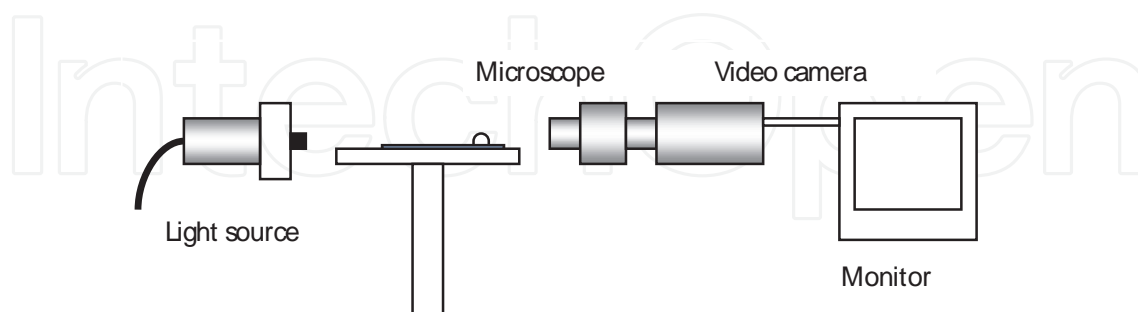
**Figure 1.** Contact angle measuring system

Contact angles of the two liquids on PU films with no UVO treatment and with maximum UVO treatment at 600 seconds are shown in Figure 2. It is clear that after UVO treatment, the water contact angle is dramatically reduced from ~70° to ~18°. For the non-polar CH_2I_2, with UVO treatment, the contact angle is moderately increased from ~16° to ~39°.
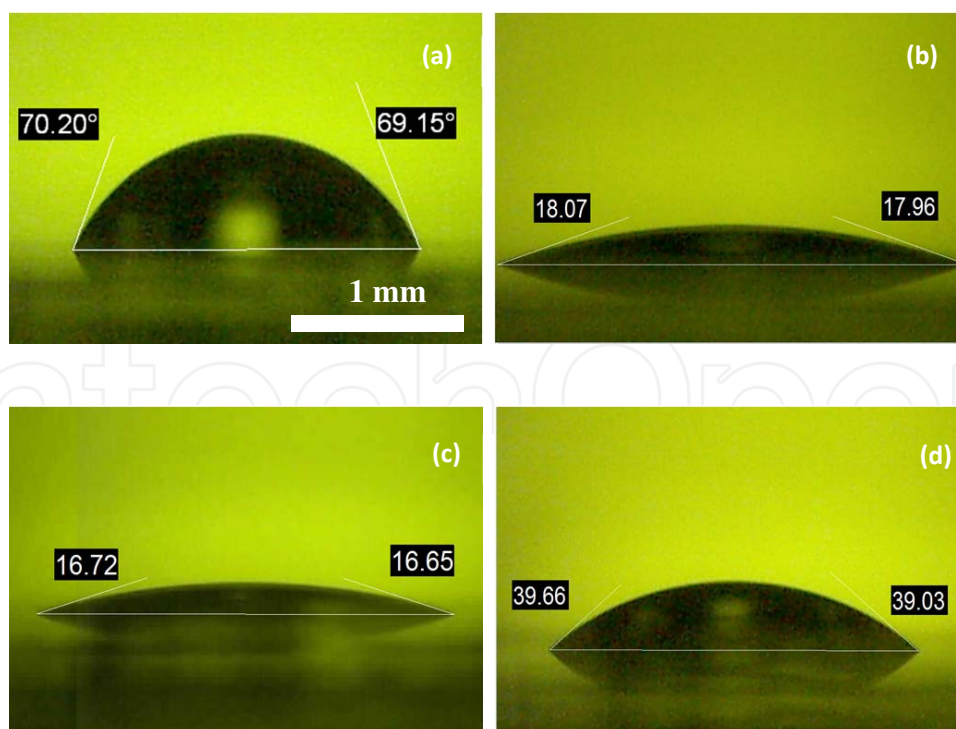
Figure 2. Contact angle images of (a) DI water droplet on non-treated PU film, (b) DI water droplet on 600sec UV-ozone treated PU film, (c) CH_2I_2 droplet on non-treated PU film, and (d) CH_2I_2 droplet on 600sec UV-ozone treated PU film

UVO time	0sec	10sec	20sec	40sec	60sec	80sec	100sec	300sec	600sec
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

Table 2. Average values of contact angles (degrees) on PU films with different UVO treatment times
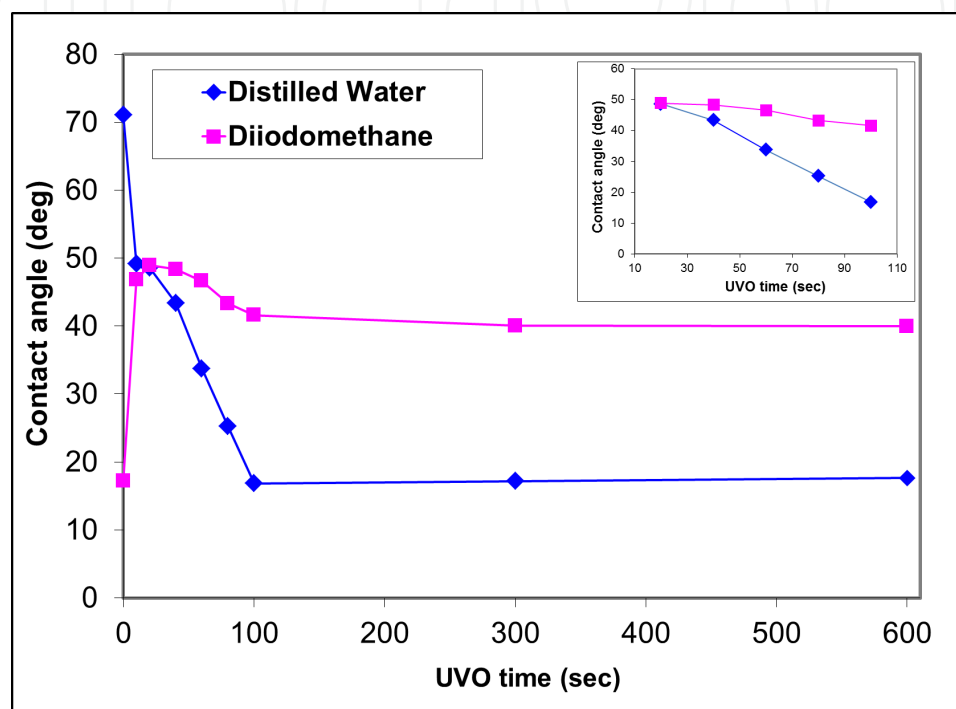
Figure 3. Contact angles of distilled water and diiodomethane on PU films (Insert shows the middle regime when UVO time is between 20 and 100 seconds)

For quantitative study, values of the average contact angles for two liquids, distilled water, and diiodomethane, on PU films with various UVO treatment times, were measured and tabulated in Table 2. The UVO treatment times were chosen as intervals from 0 to 600 seconds for different samples to determine the saturation time. Each sample was only treated once for the specific UVO treatment time. At least three data sets (three droplets) were taken for each sample, which consisted of both left and right angles. Therefore, at least six contact angle values for each UVO treatment time were recorded and the average value was used for data analysis. For distilled water droplets on the PU surface, the contact angle is 71.04º before any UVO treatment. Therefore, without any surface modification, the PU surface is close to hydrophobic and the water droplets only partially wet the surface. Values measured here are within the range of contact angles reported in the literature, which vary between 65º and 75º for this system [16, 17]. When the PU surface is UVO treated, the water contact angle decreases. It was found that as the UVO treatment time was increased, the contact angle of distilled water decreases continuously, up to a point. Therefore, the PU surface becomes less hydrophobic

and more hydrophilic. In contrast, before UVO treatment, the contact angle is 17.2º for the diiodomethane liquid. Hence, diiodomethane wets 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 less than 2º for distilled water and 1º for diiodomethane.

The contact angles for both DI water and diiodomethane on PU are plotted in Figure 3 for different UVO treatment time. Even at a very short UVO treatment time (10 seconds), the contact angles were changed significantly for both liquids (an increase of ~30º for diiodomethane and an increase of ~22º for DI water). This implies that in the very beginning of the UVO exposure, when the PU film was placed in the UVO chamber, the ozone quickly reacts with the PU surface and changes its surface chemical composition immediately. For DI water liquid, when 20-second UVO treatment was carried out on a different PU film, the contact angle was further reduced but at a slower rate. This is because the ozone reaction on the PU surface is very quick and reaches its maximum effect within a very short period of time (< 20 sec), and the decrease in contact angle is not proportional to the ozone exposure time. However, for longer UVO exposure times, for example, between 20 and 100 seconds, it can be seen that there is a linear relationship between the DI water contact angle and the UVO treatment time (Fig. 3 insert). This is mainly due to the effect of UV light radiation on the PU surface. Because the UV light dose is linearly proportional to exposure time, the PU surface chemistry is altered in the same fashion. In contrast, when the UVO exposure is less than 20 seconds, the ozone reaction is dominating so the linear correlation between the time of UV light radiation and the DI water contact angle cannot be clearly seen. However, for the treatment times between 20 and 100 seconds, UV light radiation becomes the dominant source for UV surface chemistry modification, and the decrease in contact angle is linearly proportional to the treatment time, with the water contact angle reaching the minimum of ~ 17°. For UVO treatment times greater than 100 seconds, the PU surface is completely changed by both ozone molecules and UV light, and the contact angle remains at ~ 17°. On the other hand, for the diiodomethane liquid, the contact angle at first increases from 17.2° to a maximum value of 48.9° with 20-second treatment time. This indicates that the ozone gas also has the maximum effect on the PU surface and the effect is saturated within 20 seconds. Also, the PU film surface becomes less wettable for diiodomethane. However, for UVO treatment times between 20 and 100 seconds, the contact angle of diiodomethane droplets decreased as the treatment time increased, and the decrease is also linearly proportional to the treatment time. This indicates that the PU surface also becomes more wetting for diiodomethane after longer UV light exposure. However, the rate of decrease is lower than that of DI water, and the contact angle approaches the constant value of ~ 40° for UVO treatment greater than 100 seconds, when the UVO treatment effect is saturated.

Therefore, we can conclude that there are three regimes in UVO treatment on PU surfaces. The first stage (< 20 seconds) is when the ozone effect is dominant. For the second stage, the ozone effect diminishes and a linear UV effect takes over (20–100 seconds). Finally, in the third stage, the PU surface is fully treated (> 100 seconds).

1.2. PU surface free energy calculation

For a liquid droplet on a solid surface in equilibrium, the contact angle can be calculated by the well-known Young's equation:

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

where θ is the contact angle, γ_{sv}, γ_{lv}, and γ_{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. Furthermore, Owens and Wendt proposed a general equation for calculating the surface free energy of solids based on Young's equation, which can also be applied for low surface energy materials such as polymers [18]. It can be seen that the surface tension at the solid–liquid interface, γ_{sl}, can be eliminated for the calculation from the equation:

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

where γ_{lv}^d, and γ_{lv}^h are the dispersive component (non-polar) and hydrogen bonding (polar) component of the surface energy of a given liquid against vapor, respectively $\left(\gamma_{lv} = \gamma_{lv}^d + \gamma_{lv}^h\right)$, and γ_{sv}^d, γ_{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, $\left(\gamma_{sv} = \gamma_{sv}^d + \gamma_{sv}^h\right)$. The surface free energy of the PU film with different UVO treatment times can be calculated, since the component and the total surface free energy values are known for two liquids (Table 3), and the contact angle for each liquid droplet on PU surface at different UVO treatment time was measured. The total surface energies for PU films at different UVO treatment times, as well as their dispersive and hydrogen component, are plotted in Figure 4. For PU film without any UVO treatment, the total surface free energy is 51.5 mN/m, and the dispersive and hydrogen component of the surface energy is 46.1 mN/m and 5.4 mN/m, respectively. Without any treatment, the PU surface consists of long-chain molecules and minimum amount of high energy hydrogen bonds and other radical groups. Therefore, the hydrogen component of the surface free energy is very small, and polar liquids, such as water, will not wet the surface well when they are placed in contact with PU. On the contrary, the contact angle of diiodomethane on a non-treated PU surface is very small (~17.2°). This is because diiodomethane is a non-polar liquid, so it easily wets the untreated, non-polar PU surface, which has a high dispersive (non-polar) component value. As soon as the PU film is placed into the UVO chamber (UVO time < 20 seconds), the ozone molecules immediately reacts with the PU molecules on the film surface, leading to a significant increase of the radical

groups with hydrogen bonds. The direct result is an increased hydrogen component and a decreased non-polar component of the surface free energy. Chain scission at the PU surface happens quickly and the long chains of polymer molecules are broken by the highly reactive ozone gas. Therefore, a large number of high-energy polar bonds of the broken chains are generated and exposed on the surface. The direct result is a much improved wettability for DI water, which is evident by the much smaller contact angle. In contrast, when non-polar liquids such as diiodomethane are placed on the treated PU surface, the polymer surface is less wetting. In addition, the number of long chain molecules decreases as more polar ends and hydrogen radical groups are generated on the PU surface. Therefore, the dispersive component of surface free energy decreases. For UVO treatment time 20–100 seconds, when the PU surface is modified mainly by the UV radiation, the hydrogen component (23.2–39.1 mN/m) also increases linearly, corresponding to the linear decrease of the DI water contact angles. Similarly, the small increase in the dispersive component (30.1–32.5 mN/m) corresponds to the decrease of diiodomethane contact angles (Fig. 4). Increases in both components indicates that the UV ozone improves both van der Waals interactions and hydrogen bond interactions between the solid and liquid. At UVO treatment time longer than 100 seconds, the PU surface is completely modified and the surface free energy reaches the maximum value of 71.5 mN/m, which is an 38.8% increase compared to an untreated PU surface.

| Liquid	γ_{lv}	γ_{lv}^d	γ_{lv}^h
Water	72.8	21.8	51.0
Diiodomethane	50.8	50.4	0.4

Table 3. Surface tensions (in mN/m) of the two testing liquids [19]
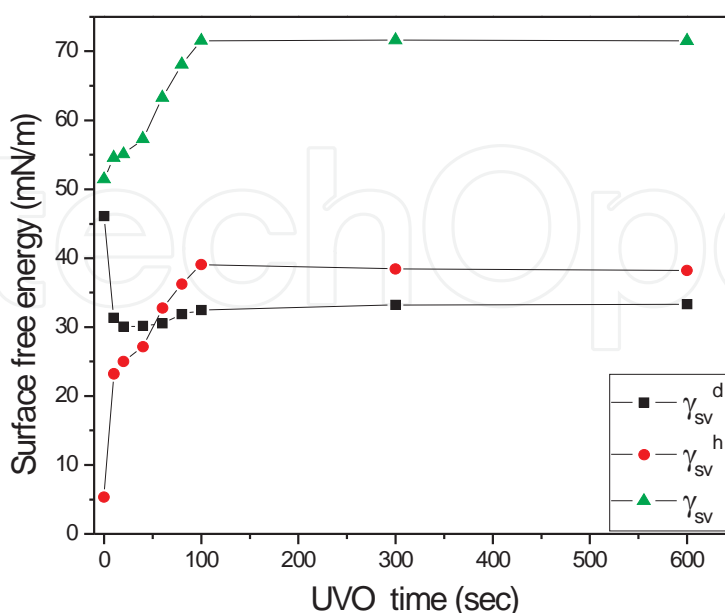
Figure 4. Surface energies of PU solid films at different UVO times

1.3. Characterization of surface chemistry change

In order to better understand the change in the PU surface by UVO treatment, an XPS study was done for untreated and 5 min UVO treated PU films. Low resolution scans of both films have the characteristic peaks corresponding to carbon (C 1s), oxygen (O 1s), and nitrogen (N1s) (scans not shown) [20]. Furthermore, the scans show additional peaks corresponding to sulfur (S 1s), which is a common element in typical polyurethane. It also shows that, after 5 minutes of UVO treatment, the oxygen level on the PU surface was considerably increased.
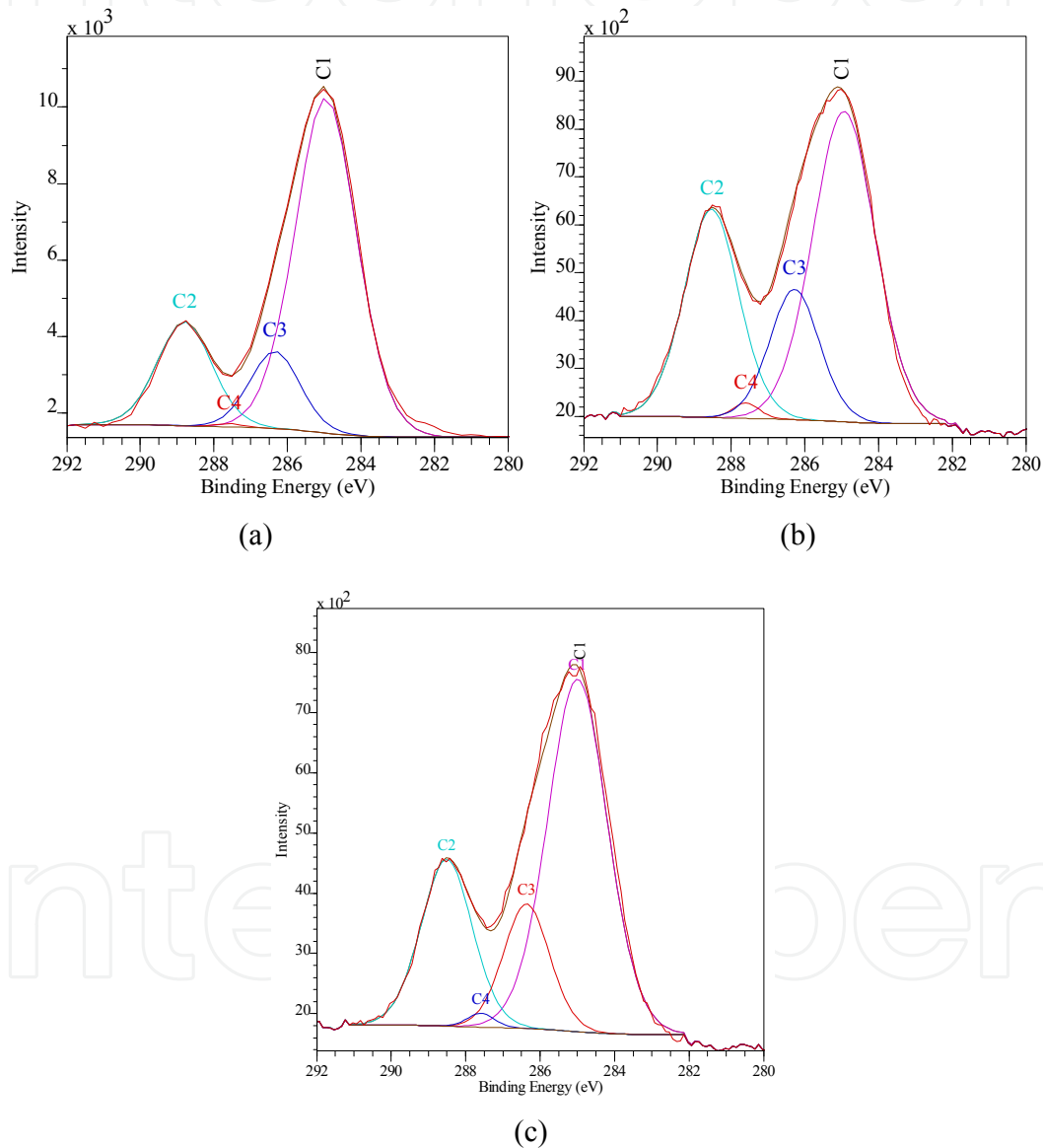
Figure 5. High resolution XPS spectra showing the deconvoluted C1s envelopes for (a) untreated polyurethane film and (b) 5 min UVO treated PU film, and (c) 5 min UVO treated PU film after washing

For detailed chemical analysis, Figure 5 (a) and (b) show the high-resolution spectra of the O 1s peaks for the untreated PU film and the 5min UVO treated PU film. The C 1s spectrum of

the untreated PU film can be deconvoluted into four sub-peaks (Fig. 5(a)) [20]. The high-resolution spectra of the C 1s peaks for the samples were plotted in Figure 5 for further surface chemical characterizations. The C 1s spectrum of the untreated PU film can be deconvoluted into four sub-peaks (Fig. 5(a)) [20]. The peak at the lowest binding energy (285.0 eV) corresponds to (-C-C-) and (-C-H-) bonding (denoted **C1** in Fig. 1). The (-N-CO-O-) group corresponds to the second peak (**C2**) and is located at around 288.5 eV [4]. The third 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)). For the 5 min UVO treated PU surface, the oxygen-carbon double bonding (**C2**, **C4**) and single bonding (**C3**) peaks are much higher than those of the untreated PU surface. The significant increase of the oxygen content in PU surface is the direct result of UV ozone treatment, which breaks the long chain molecules, and atomic oxygen or ozone gas readily react and form oxygen-carbon single and double bonding groups. For the 5 min UVO treated PU, the number of oxygen-carbon bonding groups is saturated. Therefore, the XPS spectrum shows the maximum intensity of the peaks for various oxygen-carbon bonding species. The quantitative studies of the different species are shown in Table 4.

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**

Table 4. Surface composition (area %) of untreated and 5 min UVO treated polyurethane thin films

Table 4 shows the surface chemical compositions for both untreated and treated PU films, represented by the integrated XPS intensity areas under each peak. The area of **C1** is reduced from 68% to 51%, while the areas of **C2**, **C3**, and **C4** increase for the 5 min treated sample. For comparison, the ratio of the areas of (C-O) and (C=O) bonds to the area of the (-C-C-) bonding (**C1/C2** and **C1/C3**) was taken for both samples. The ratio of the integrated areas **C1/C2** and **C1/C3** were 3.66 and 5.39, respectively, for the untreated sample. This is because carbon–carbon bonding is the dominant species on the pristine polyurethane surface. For the 5 min UVO treated PU surface, the ratios of **C1/C2** and **C1/C3** were reduced to 1.71 and 2.98, respectively. Therefore, the C-C bonds were reduced by about 50% after 5 min UVO treatment. The decrease in the area ratio after UVO treatment also implies the amount of C-O and C=O bonding species is increased. The increase of hydrophilic carbon-oxygen bonds is the main reason for the increased wettability of the PU films.

1.4. Surface morphology change by UVO

The 5μm x 5μm 3D AFM images in Figure 6(a) and (b) show the surface morphology of as-prepared, untreated and 5 min UVO treated PU films, respectively. The AFM image shows a

very smooth surface morphology for the pristine PU surface. The area roughness study showed the root mean square roughness, R_{rms}, was 0.392 nm. The 5 min UVO treated sample showed a different surface morphology. The z-axis of the 3D image is 20 nm, compared to the 6 nm for the untreated sample. It shows many straight pillars with a height of around 3–8 nm. The R_{rms} was also increased significantly to 2.073 nm, more than 5 times rougher than the untreated sample. The pillars are low molecular weight oxidized species and possibly the tips of broken chains of PU molecules created after UVO exposure. The AFM images (Figure 6) were taken within 1 hour of the 5 min UV ozone treatment in a dry environment. Therefore, the low molecular weight oxidized species could still be observed. It is intuitive to state that, from previous studies of different short UVO treatment times (Table 2), as the UVO treatment time increases (10–100 sec), 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° to 17°). At treatment times longer than 100 sec, the low molecular weight oxidized species are saturated on the PU film surface, and the water contact angle stabilizes around 17°. Furthermore, the low molecular weight oxidized species can be identified in the XPS plot, which shows the fraction of oxygen-containing species is significantly increased for the 5 min UVO treated samples. Therefore, the oxygen groups (**C2**, **C3**, and **C4**) are created by the UV ozone where chain scission takes place and oxygen-containing free radicals are formed, and they are observed as straight pillars in the AFM image.

The advantage of UVO treatment is that it does not physically remove material from the surface. This is preferred to oxygen plasma etching, which can remove a significant amount of material [20]. UVO treatment only affects the surface of the PU film by breaking the long chain (-C-C-) bonds and inserting 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 non-destructive surface modification method provides another simple and economical approach for polymer surface wettability functionalization.

1.5. Effect of ultrasonic washing for the UVO treated sample

The effect of water washing on the UVO treated PU film was also characterized. Similar studies have been done for other polymer materials with UVO treatment on the surface [10]. In this study, for a polyurethane film surface with 5 min UVO treatment, the sample was immediately placed in an ultrasonic DI water bath for 5 minutes right after UVO treatment. The sample was then dried by blowing air, and characterization was carried out within an hour. As shown in Figure 5 (c), the XPS spectrum of the washed sample has the same carbon (C 1s) peaks as the untreated sample and the 5 min UVO treated sample without washing. Compared to the treated sample without washing (Fig. 5(b)), the intensity of the peaks for oxygen-containing species (**C2, C3**) is considerably reduced for the washed sample. When compared to the pristine PU surface (Fig. 5(a)), the intensity of those peaks is still noticeably higher for the washed sample. Table 4 shows the quantitative surface composition study and indicates the **C1** area is increased to ~59% for washed sample, compared to 51% for the treated sample without washing. **C1/C2** and **C1/C3** ratios of the integrated areas were 2.46 and 3.66, respectively. This indicates that some of the low molecular weight oxygen-containing species created on the PU
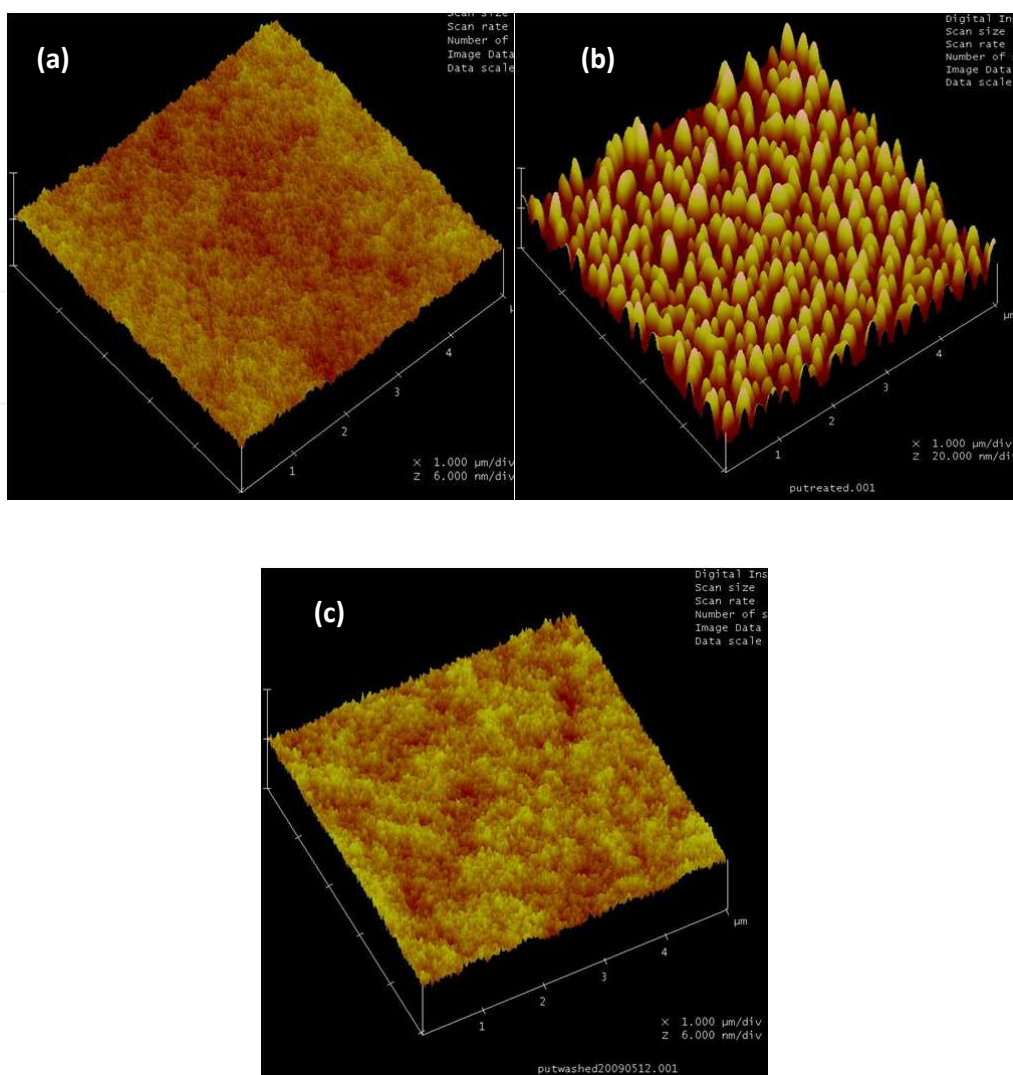
Figure 6. The 5μm×5μm 3D AFM images of (a) untreated polyurethane thin film with rms roughness *w*= 0.392 nm, (b) polyurethane thin film treated by 5 min UV ozone with *w*=2.073 nm, and (c) 5 min UV ozone treated PU thin film after washing with *w*=0.321 nm.

surface by UV ozone treatment were removed by water washing. Nevertheless, the washed sample still shows more oxygen content in the XPS spectrum than the untreated sample, and the oxygen content level is sustained days after washing. Furthermore, the AFM image of the UVO treated sample after washing is shown in Figure 6(c). Indeed, the surface roughness of the washed sample is quite similar to that of the pristine PU surface, and R$_{rms}$ is 0.321 nm, which is slightly lower than that of the untreated sample. This is because the low molecular weight oxidized species have been dissolved and removed by washing in the ultrasonic DI water bath, which resulted in a flat, smooth PU surface, as observed by the AFM studies. The XPS results confirmed that the oxygen content levels on the PU surface for the washed sample were lower than for the UVO treated sample. The DI water contact angle for the washed sample was ~48°, which is higher than the UVO fully treated sample (17°, Table 2), but it is still lower than the PU films without UVO treatment (70°).

1.6. Hydrophobic recovery

Aging of the UVO treatment on PU surfaces was also investigated to study the hydrophobic recovery. The DI water contact angles on 5 min UVO treated PU films were measured at different aging times under ambient conditions (Fig. 7). The DI water contact angle on a 24 hour old PU film was 17.2º, which was nearly the same as the contact angle measured immediately after the UVO treatment (dotted line, Fig. 7). The contact angle increased to 19.8º after 2 days of aging and reached a constant value of about 21–22º after 3 days. Nevertheless, the increase in the water contact angle is negligible, since the contact angle for the untreated PU films is significantly higher at ~70° (Fig. 7 dashed line). This implies that the effect of UVO treatment is sustained with much improved wettability, and the hydrophobic recovery is insignificant. This is because in polar and hydrophilic species, the single and double carbon-oxygen bonds stay intact on the PU surface permanently after UVO treatment. It was also noted that the transparent PU film yellowed after the 5 min UVO treatment, but the yellow color disappeared after a few days. The yellowing effect is possibly caused by the high UV light exposure on the PU surface during the UVO treatment.
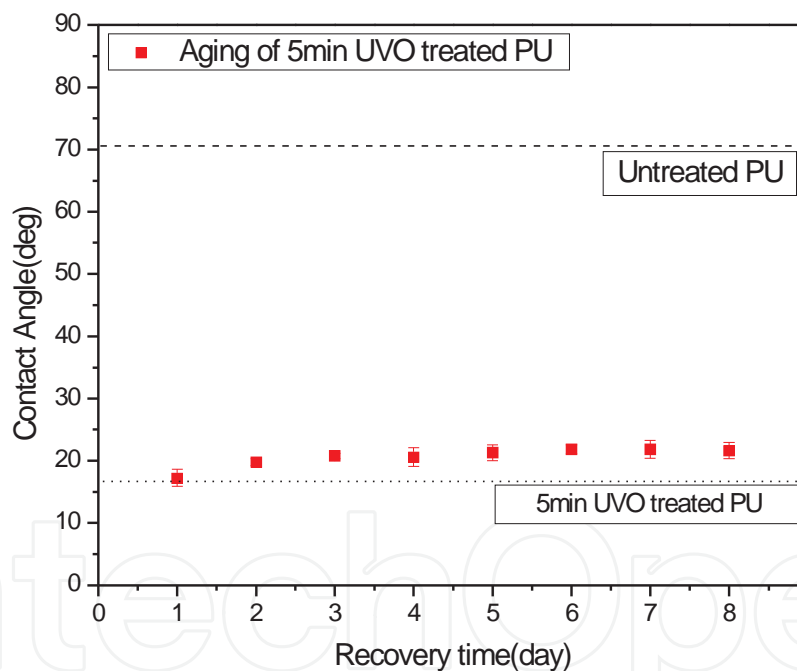
Figure 7. Change of the water static contact angle values versus aging time for polyurethane thin films after 5 minutes of UV ozone exposure

1.7. Wetting on PU grating structure

Microstructures with increased surface area and modulations possess more complicated surface wetting properties than flat surfaces. In general, due to the topography, such structures tend to be more hydrophobic with much larger apparent contact angles for different liquids. It is of particular interest to understand and manipulate the surface wettability of complex

structures for specific surface wetting needs. Surface treatment on polymeric structures can increase the surface free energy and, thus, improve the wettability. For this investigation, a one-layer (1L) PU grating structure with 2.5 µm periodicity and 1:1 aspect ratio were fabricated by microtransfer molding (Fig. 8). The water contact angle on the 1L PU grating is increased significantly to ~138° (Fig. 9 (a)) compared to ~70° of the PU flat surface. This indicates the PU grating has become much more hydrophobic due to the surface corrugation, approaching a superhydrophobic state. Such a hydrophobic surface poses as a serious problem for complete conformal wetting of the surface and for removal of air gaps and liquid infiltration of gratings. After UVO treatment (720 sec) was carried out on the 1L PU grating structure, the water contact angle was reduced to ~67°, and the surface has changed from hydrophobic to hydrophilic state. This is mainly caused by increased surface free radicals and polar bonds on the polymer chains on the PU grating surface. Hence, the water droplet spread out and easily penetrated into the trenches of PU gratings. It has been shown that this surface treatment can benefit the infiltration of liquids into 3D microscale polymeric molding structure [21]. Therefore, UVO treatment can be a simple and economical surface modification method for various surfaces and structures.
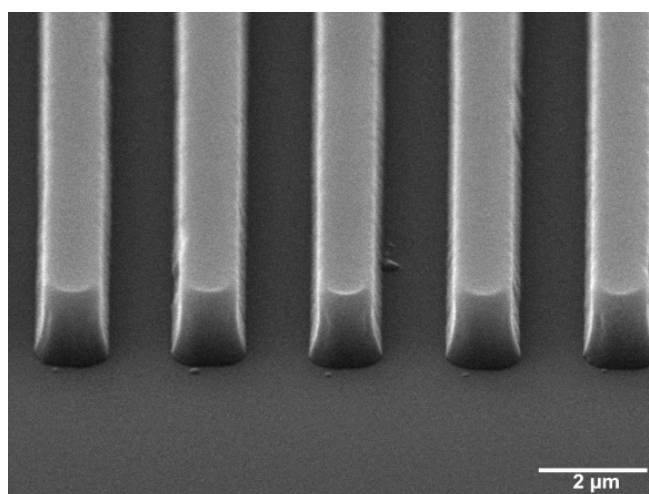

Figure 8. SEM image of a 1L PU grating structure with 2.5 µm periodicity and 1:1 aspect ratio
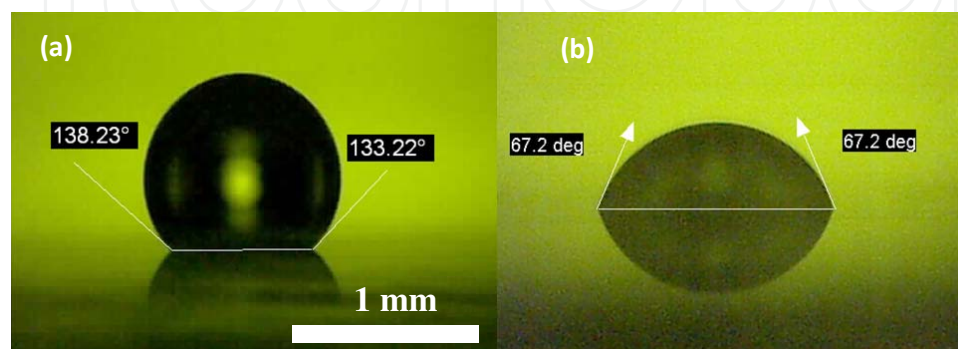

**Figure 9.** Water contact angles of 1L PU grating (a) without UVO treatment and (b) with 720 sec UVO treatment

1.8. Polyurethane fibrillar tip array as bio-inspired adhesives

Recently, a microstructured PU surface has been investigated for improved wettability and adhesion for novel applications using UVO treatment [22, 23]. Animal perching systems are being mimicked to realize similar locomotion capabilities for landing on rough or smooth surfaces with various inclinations. Bio-inspired adhesives comprising fibrillar arrays are similar to those used by geckos, spiders, and flies. Fibrillar bio-inspired adhesives provide high adhesion against a great variety of surfaces with different moisture conditions. Such microscale fibrillar structures can be easily fabricated using standard soft lithography techniques with polymeric elastomers such as polyurethane (Fig. 10). Subsequently, the fibrillar tips are enlarged by an "inking process" [23].

a   **b**
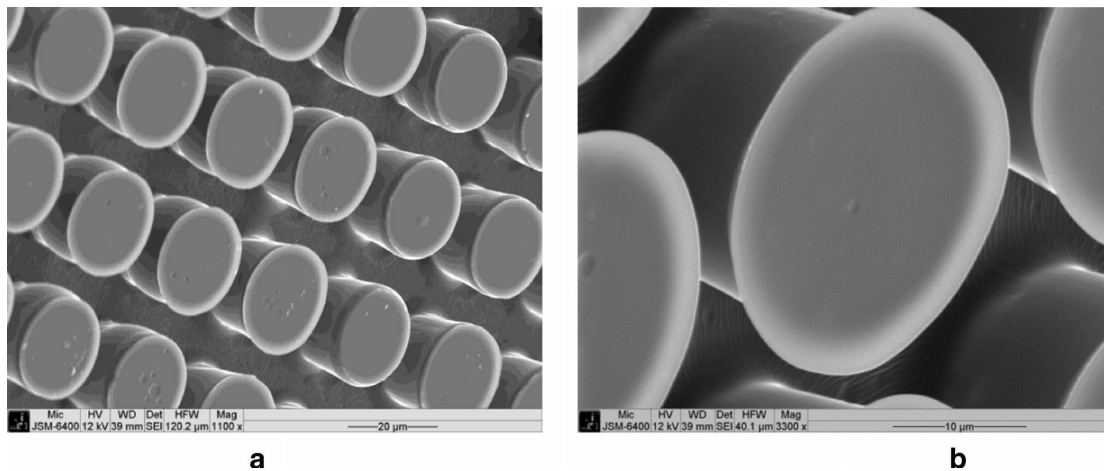
Figure 10. (a) SEM image of the polyurethane fibrillar array integrated into the perching/bio-inspired adhesion mechanism, (b) higher magnification of fibril enlarged tip [23] (Permission from reference 23)

The fibrillar arrays are hydrophobic in nature due to the low surface energy of PU surface and its surface corrugation. Surface treatment is necessary to improve its wettability and increase its surface free energy for better adhesion. In this reference, PU flat films exhibit similar wettability for water as illustrated in section 1 of this work, where the water angle is ~70° before UVO treatment and <15-17° after UVO treatment. For the fibrillar array patterns, the water contact angle is ~120° before UVO treatment. With UVO treatment, the water contact angle is significantly reduced to ~15-17° as well (Fig. 11 (a)). Unlike the flat PU film, the shear and tensile adhesion capacities of PU fibrillar arrays after UVO treatment were also enhanced significantly acting as bio-inspired adhesives. For demonstration, a perching system was made with the UVO treated fibrillar arrays placed on top of four flat elastomer pads, which were attached to the toes of four shape memory alloy (SMA) wires. The perching system was placed at a flat and smooth polyethylene sheet surface and then inclined at 75° with respect to the horizontal direction. The system can be sustained on the surface without falling off even with a 20 gram mass.
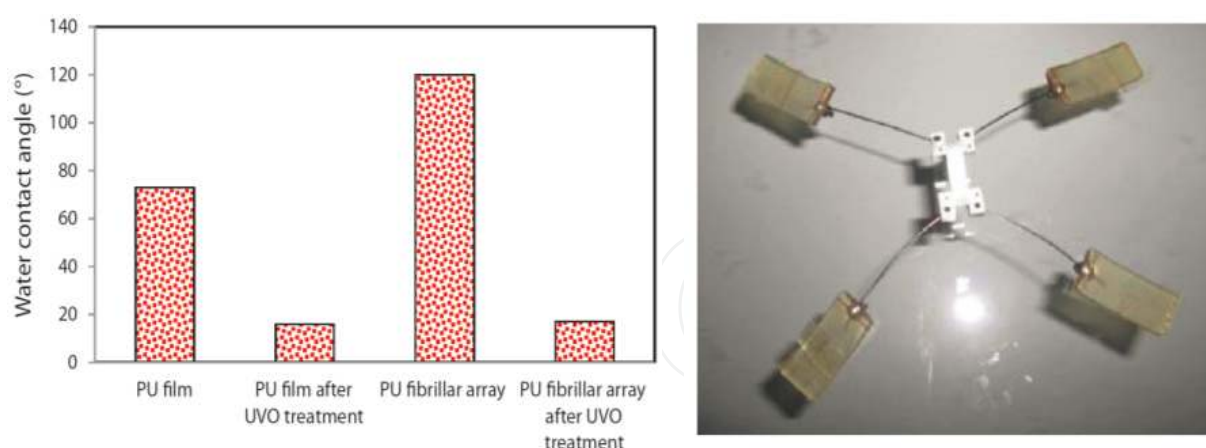
Figure 11. (a) Water contact angles of PU plain film and fibrillar array prior to and after UVO treatment. (b) Perched system with PU fibrillar array on four elastomer pads adhered to a smooth polyethylene sheet inclined at 75° with respect to the horizontal direction [23]. (Permission from reference 23)

2. Conclusion and summary

Studies have shown that, by using UVO treatment as a surface modification method, the wettability of polyurethane film surface can be significantly improved. The two liquids tested in this study showed different wetting phenomena. It was observed that, in the very beginning of the UVO treatment (< 20 seconds), the ozone gas molecules had an immediate effect on the PU surface and the contact angle for DI water was noticeably reduced. In the second stage of the UVO treatment (20–100 seconds), the UVO effect is linearly related to the treatment time, and the contact angles for both testing liquids decrease in a linear fashion until the PU surface is fully modified. Both polar and non-polar interactions between the liquids are improved by the UVO treatment in the second stage, and the total surface free energy of the PU surface is increased linearly until it is fully treated. The total surface free energy of a fully treated PU surface is 71.5 mN/m, which is a ~38.8% increase over the untreated PU surface. XPS analysis shows significant hydrophilic C-O and C=O bonding species were created on the PU surface by UVO treatment, which is the cause for higher surface free energy and improved surface wettability. Surface morphology study by AFM shows the PU surface roughness is increased by UVO treatment with increased amount of low molecular weight oxidized species and broken ends of long chain molecules, which can be removed by strong agitation such as water washing in ultrasonic bath. But the oxygen content on the washed sample is still higher than a pristine PU surface. Additional experiments with distilled water were also conducted for one-layer PU grating molds (2.5µm pitch) made by the micro-transfer molding (µTM) technique. It was shown that on the structured non-treated one-layer PU mold, hydrophobic wetting occurred and the contact angle of a water droplet was about 138 degrees. When sufficient UVO treatment was done on the mold, the water droplet had a much smaller contact angle and was pulled into the channels because of the improvement on the wetting characteristics of the PU mold. This opened up a door for future studies on the infiltration of aqueous

slurry into 3-D polymeric structures at micro-size, and for improved adhesion for novel applications [21, 23].

Acknowledgements

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