

Surface Modification of Siloxane Containing Polyurethane Polymer by Dielectric Barrier Discharge at Atmospheric Pressure

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ABSTRACT: Surface treatment of polymers by discharge plasmas is of great and increasing industrial application because it can uniformly modify the surface of treated samples without changing the material bulk properties. Present work deals with surface modification of siloxane-containing polyurethane (PU-Si) by air dielectric barrier discharge (DBD) at atmospheric pressure. Material characterization was carried out by contact angle measurements, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). The surface energy of the polymer surface was calculated from contact angle data using Owens-Wendt-Kaeble method. The plasma-induced chemical modifications are associated with incorporation of polar oxygen con-

taining groups on the polymer surface. The AFM analysis of DBD-treated samples revealed that the surface roughness decreased with increasing the time of treatment. Because of the plasma exposure the surface of DBD-treated polymers became hydrophilic resulting in enhanced adhesion properties. Aging behavior of the treated samples revealed that all polymer surfaces were prone to hydrophobic recovery; however, they did not completely recover their original hydrophobic characteristics. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: dielectric barrier discharge; surface modification; polyurethane; wettability

INTRODUCTION

Thermoplastic polyurethane-based polymers have found increasing number of applications in modern technology because of an excellent balance between their mechanical, thermal, and chemical properties combined with good biocompatibility.¹ Because of their high flexibility the polyurethanes are widely used in the automobile industry as high-resiliency flexible foam seating, rigid foam insulation panels, microcellular foam seals and gaskets, durable elastomeric wheels and tires, automotive suspension bushings, electrical potting compounds, high performance adhesives, and sealants.² Polyurethane is often used in medical devices such as blood contacting devices (artificial veins or heart valves) and

long-term implants such as urethral catheter, breast implants, or pacemaker leads.³ To improve PU mechanical properties the common PU polymers are frequently mixed with siloxane elastomers.^{4,5} The effect of silicon concentration on the performance of PU has been investigated in the literature showing that the PU-Si copolymers exhibit superior mechanical properties and great biocompatibility.^{6,7} However polyurethanes, and especially the PU-Si polymers present very low surface energy, which results in poor adhesive properties.⁶ For many industrial and biomedical applications the surface characteristics of these materials have to be improved without changing the advantageous bulk properties. In the past decade, plasma treatments have demonstrated to be very efficient in modifying the surface wettability of polymers. Some previous works investigated low-pressure plasma treatments of commercial polyurethane^{2,8,9} and medical grade polyurethane^{3,6,10–12} reporting significant improvement of surface wettability after the plasma exposure. Recently the atmospheric plasma processing of polymeric materials¹³ has attracted significant attention because it has additional advantage of being cheap and easy to scale and implement in industrial processing. Yet,

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few authors^{14,15} have studied the effect of nonthermal plasmas on PU polymers at atmospheric pressure. One of the most promising atmospheric plasma sources for material processing is based on the dielectric barrier discharge (DBD). DBD is a type of discharge, which occurs between two planar or cylindrical electrodes, providing that at least one electrode is covered by a dielectric layer, i.e., it is not in direct contact with the gas. The consequence of this arrangement is that, after the gas breakdown, the charge accumulation on the dielectric surface prevents the corona-to-arc transition and, eventually, stops the discharge if the voltage does not increase continuously. Usually AC voltages of few kV at frequencies between 50 Hz and 500 kHz are used to create an active discharge region. The DBD plasma generally consists of a large number of randomly distributed microstreamer discharges. Each streamer has typically a few nanoseconds in duration and a few μm in diameter.¹⁶ The mean electron energy in DBD plasmas is in the range of 1–10 eV, while the chemical binding energy of polymers is less than 10 eV. Therefore, energetic particles and UV photons in DBD can easily break the chemical bonds of polymers and active radicals abundant in the plasma react with dangling bonds on the surface thus modifying the material wetting properties.¹³

The present work deals with surface modification of polyurethane-siloxane polymer by atmospheric pressure DBD in air. Material characterization was carried out by contact angle measurements, surface energy evaluation, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Materials

Many researchers have been interested in the properties exhibited by siloxane containing copolymers, such as very low surface energies, hydrophobicity; good thermal stability; high gas permeability; biocompatibility, low dielectric constant, and low solubility.^{4–7} In this study, segmented siloxane-polyurethane (PU-Si) polymer was provided by the PerkPlast Industry, Brazil in the form of 1.5-mm-thick film. The material was synthesized from polydimethylsiloxane (PDMS) by step growth polymerization. The PDMS content of the PU-Si copolymer was kept around 30 wt %.

Preparation of the samples

The PU-Si samples, cut into rectangular shape ($10 \times 15 \text{ mm}^2$), were ultrasonically cleaned in distilled water and detergent for half an hour. After that to

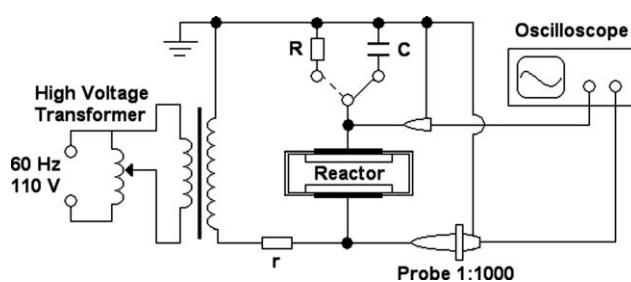


Figure 1 Schematic drawing of the experimental setup.

remove organic contaminants from the surface, the samples were washed in isopropyl alcohol for 10 min and then dried at room temperature. Before the plasma processing the samples were placed on the bottom electrode of the DBD reactor schematically shown in Figure 1.

Plasma treatment

The experimental arrangement used to generate air DBD discharge at atmospheric pressure is sketched in Figure 1. The DBD discharge is generated between two 9.5-cm-diameter parallel aluminum electrodes positioned within a 150-mm-diameter cylindrical enclosure made from Delrin[®]. Both reactor electrodes were covered by 0.5-mm-thick polyester (Mylar[®]) film. The upper electrode was grounded while the lower one was employed as high-voltage electrode. For all DBD treatments the distance between the two electrodes was fixed at 4 mm. The high-voltage power supply is consisted of a step-up high-voltage transformer (110/20,000 V, 60 Hz) driven by an autotransformer Variac. A load resistor of 1 k Ω protected the transformer in case of DBD to arc transition. All plasma treatments were carried out in air at atmospheric pressure and ambient temperature.

The AC voltage applied to the reactor lower plate was measured by a 1000:1 high-voltage probe (Tektronix P6015A, 75 MHz) and monitored on a digital oscilloscope (Tektronix TDS 2024B, 200 MHz). For displaying the waveform of the discharge current on the oscilloscope the reactor upper plate was grounded through a current measuring resistor of 120 Ω . The charge Q on the reactor plates was obtained from the voltage drop across a serial capacitor of 0.91 μF .

A simple method for obtaining the discharge power of DBD reactors relies on so-called Lissajous figures. They are obtained when plotting transported electric charge Q through the discharge as a function of the applied periodical voltage.¹⁷ The average electric energy dissipated in one discharge cycle is simply the area of the characteristic Q - V diagram. Then the mean discharge power is calculated by

multiplying the discharge energy to the frequency of the AC power supply.

Characterization techniques

The contact angle between a test liquid and the polymer surface was obtained by the sessile drop method on a standard Rame-Hart goniometer, model 290 using the DROPImage software. The measurements were carried out in controlled environment with 60% relative humidity and temperature of 21°C. The volume of each liquid drop was 2 μL and two different test liquids: water and diiodomethane were used. At least five different drops were deposited on the polymer surface to obtain the average value of the contact angles. The maximum error in the contact angle assessments did not exceed 3%. Surface energies were calculated by using the Owens–Wendt–Kaelble method¹⁸ on which polar and nonpolar (dispersive) contributions are considered to explain the interaction between the liquid and the solid phases.

Surface chemical characterization was carried out by X-ray photoelectron spectroscopy using a Kratos XSAM HS system. The base pressure in the analyzing chamber was kept below 10^{-7} mbar. The Mg K α line ($h\nu = 1253.6$ eV) was employed as excitation source with the emission voltage and current of the source set to 6.0 kV and 5.0 mA, respectively. The obtained spectra were processed by a code provided by the apparatus manufacturer using the Shirley method for background subtraction. All peaks were fitted using Gaussian curves. The value of 284.8 eV of the hydrocarbon C1s peak was used for calibration of the energy scale.

Atomic Force Microscopy—AFM, was used to analyze surface morphology of the polymer samples. The AFM analysis was performed in air with a Nanoscope-V Multimode atomic force microscope.

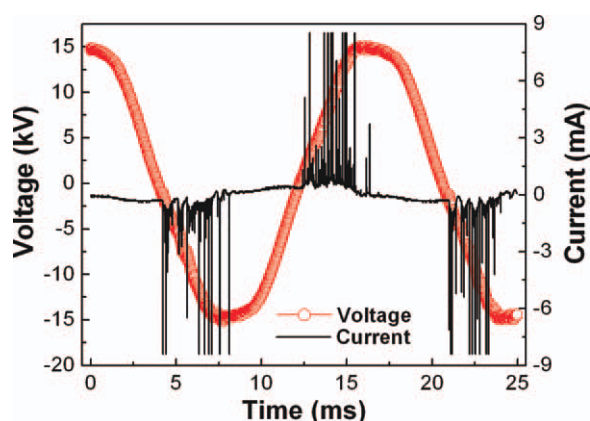


Figure 2 Typical waveforms of the discharge current and voltage. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

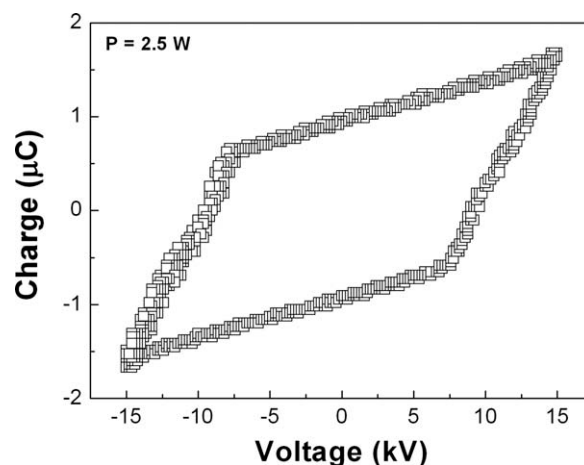


Figure 3 Q-V Lissajous figure of the parallel-plate DBD reactor.

During the analysis, the microscope was operated in tapping mode with a scanning rate of 0.5 Hz for all scanning sizes using etched silicon probe ($k = 50$ N m^{-1}). From the AFM images on 5.0×5.0 μm^2 area the root mean square roughness (r_{rms}) of the topographic profiles was evaluated. For each sample several images on different spots were acquired and after that the average value of the roughness was calculated.

RESULTS AND DISCUSSION

Figure 2 depicts the typical waveforms of the discharge current and voltage. The air DBD discharge operated in filamentary mode i.e., it was constituted by many tiny streamers randomly distributed over entire area of the dielectric barrier. Each tiny current peak in Figure 2 originates from the superposition of many microdischarges occurring at the same time. Differently from the nonuniform field DBD reactor in Ref. ¹⁹, the discharge current of the parallel-plate reactor employed in this work consists of large number of short micro-pulses instead of a large current pulse superimposed to many micropulses.

A Lissajous figure of the DBD reactor used in this experiment is presented in Figure 3. It exhibits the characteristic parallelogram shape, which is usual for parallel-plate DBD reactors.

All polymer treatments were performed in air at ambient pressure and temperature conditions. The applied AC voltage was fixed at 30.0 kV_{p-p}, which corresponded to 2.5 W of electric power (discharge power per unit area of 35 mW cm^{-2}). At fixed discharge power, the degree of surface modification was controlled by varying the treatment time.

Contact angles between droplets of distilled water or diiodomethane and polymer surfaces were measured to evaluate the surface modification of the samples. The results from the contact angle assessments

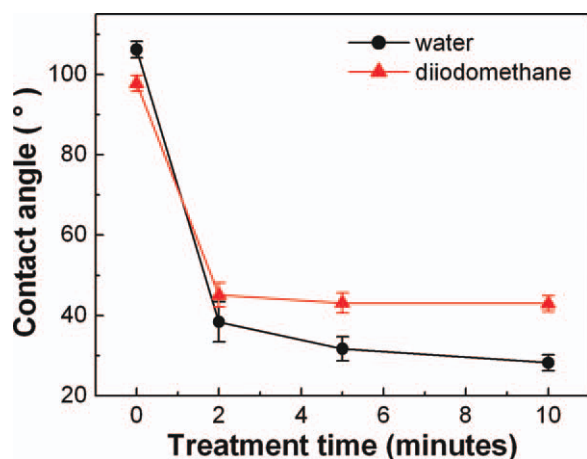


Figure 4 Water and diiodomethane contact angles of PU-Si polymers measured soon after the DBD treatment as a function of plasma exposure time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are shown in Figure 4. The plasma treatment was very efficient promoting hydrophilic characteristics to the initially hydrophobic polymer. For both testing liquids the values of the contact angle decrease sharply after 2 min of DBD treatment. For plasma exposure time greater than 5 min the changes of the contact angles become irrelevant and their values reach plateaus at about 30° for water and 43° for the diiodomethane, respectively. The considerable increase of the polymer wettability (water contact angle reduction of about 70%) suggests that large amount of polar groups was incorporated on the surface as a result of the DBD treatment.

The PU water contact angles obtained in this experiment are lower than the ones in Ref. ¹⁹ where the samples were treated in a DBD reactor with wire-duct geometry. The lower degree of PU surface modification in the latter case can be explained by the fact that the plasma in nonuniform field reactors is mostly concentrated around the low area electrode while the samples during the treatment were placed on the grounded plane electrode (6-mm away from the wire electrode) thus receiving less active species from the plasma.

It is well known that plasma-treated polymers exhibit partial contact angle recovery after the plasma surface modification.¹³ This behavior can be explained by the fact that the plasma-treated polymers try to reduce their surface energy.²⁰ This process is referred to as hydrophobic recovery or surface aging process. To study the evolution of polymer surface after the DBD treatment, the treated samples were stored in air at room temperature (60% relative humidity) and contact angle measurement using water and diiodomethane were performed during a period of 2 weeks.

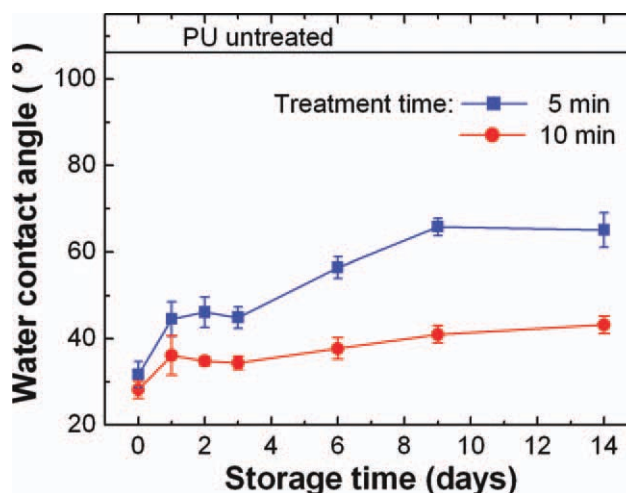


Figure 5 Hydrophobic recovery of the polymer samples treated for 5 and 10 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 shows the evolution of the water contact angle of plasma-treated PU-Si as a function of the storage time. For better comparison the water contact angle of the untreated sample ($\theta = 106.4^\circ$) is also plotted in Figure 5.

As shown in previous works^{6,7,21} the siloxane-containing polyurethanes exhibit enhanced hydrophobicity, which justifies the high water contact angle ($\sim 106^\circ$) of the pristine sample. As can be seen in Figure 5, for both DBD treatments the polymer aging process is characterized by a quick increase of the water contact angle during the first 2 days of

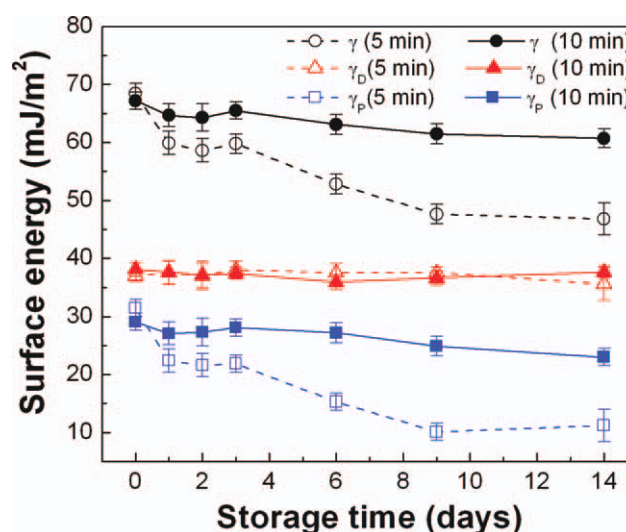


Figure 6 Evolution of the polymer surface energy and its polar and dispersive component. The hollow symbols indicate the 5-min treatment and the solid symbols correspond to the 10-min DBD treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Elemental Composition of PU-Si Polymer (atm. %)

Samples	Atomic concentration (%)			
	C	O	N	Si
Pristine	59.6	25.1	1.0	14.3
DBD treated for 10 min	45.6	37.5	1.2	15.7

storage followed by a slow recovery process during the next week. After 10 days of storage there are still small variations of the polymers contact angle; however, no significant changes were observed. Similar aging behavior of plasma treated polymer was observed in Ref.²⁰ where the authors followed the surfaces aging process during 24 days and also no significant hydrophobic recovery after the 10th day of storage was noticed. The PU-Si samples from the two plasma treatments suffer different degree of hydrophobic recovery. The samples treated for 5 min were more prone to hydrophobic recovery than the ones treated for 10 min. After 14 days of storage at ambient conditions the water contact angle of 5- and 10-min plasma treated samples tended to saturate at about 65° and 43°, respectively.

From the contact angle measurements with two different liquids the surface energy of the pristine sample was determined as $\gamma = 13.7 \text{ mJ m}^{-2}$ with a polar component of $\gamma^p = 2.2 \text{ mJ m}^{-2}$ and a dispersive component $\gamma^d = 11.5 \text{ mJ m}^{-2}$. After 10 min of plasma exposure the PU surface energy increased significantly with a polar component of $\gamma^p = 39.1 \text{ mJ m}^{-2}$ and a dispersive component of $\gamma^d = 38 \text{ mJ m}^{-2}$. The variation of the surface energy of plasma treated polymers as a function of the samples storage time is shown in Figure 6. As can be seen the surface

energy gradually decreased with the storage time reaching saturation values about 60 mJ m^{-2} for the 10-min DBD treatment and 47 mJ m^{-2} for the 5-min treatment, respectively. Because for both treatments the dispersive component of the surface energy remained practically unchanged during the whole period of storage the variation of the polar component was responsible for the surface energy reduction. Possible reasons for this polymer surface instability include the reorientation of polar groups at the surface layer and also the diffusion of unpolar groups from the bulk to the surface.^{22,23}

Two week after the DBD treatment, when the process of polymer hydrophobic recovery had already taken place, the atomic composition of the samples was investigated by XPS analysis. The elemental composition of the polymer surfaces before and after 10 min of plasma treatment is shown in Table I. Large Si content on the polymer surface comes from incorporation of siloxane units into main polymer chain during the synthesis of PU-Si polymer. Siloxane components are needed to improve the polymer properties by increasing the flexibility, cohesiveness and wear resistances.^{7,21}

Table I shows that the amount of nitrogen and silicon on the polymer surface changes very little as a result of the air plasma exposure. Because the uncertainty associated with XPS peak intensity measurement is estimated in the literature²⁴ as 15%, the small variations in the N and Si contents before and after the DBD treatments lay inside the experimental error bar.

On the other hand the DBD treatment caused an increase of the oxygen content on the polymer surface. The O/C atomic ratio increases from 0.42 for the pristine PU-Si to ~ 0.82 after the 10-min plasma

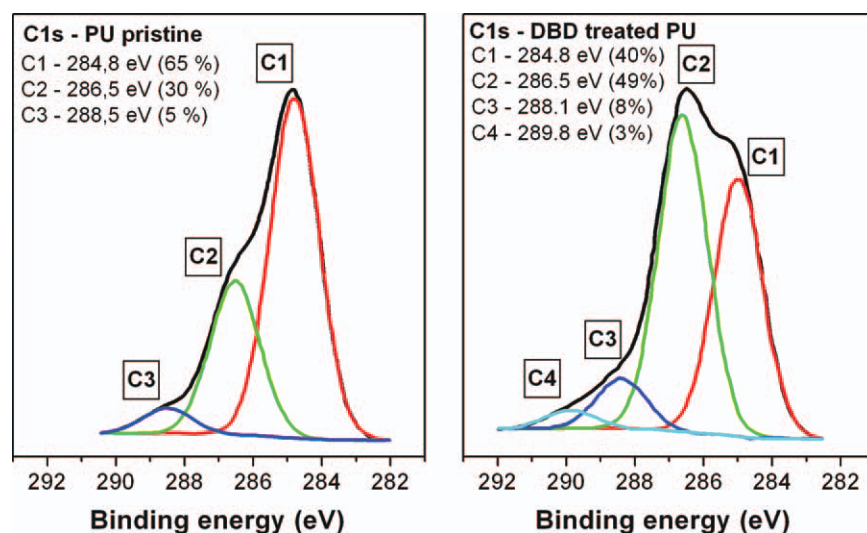


Figure 7 C1s spectra of (a) untreated and (b) DBD-treated PU-Si polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

treatment. The increased O content of the plasma-modified polymers suggests that new oxygen-containing groups are formed on the surface. Therefore one can conclude that the enhanced wettability of DBD-treated polymers is associated with the formation of polar oxygen moieties.

To determine which kind of oxygen-containing functionalities are formed on the polymer surfaces after the plasma exposure the C1s core level of the XPS spectra is investigated in details and the peaks corresponding to the untreated and the 10-min treated samples are presented in Figure 7. The C1s spectrum of the pristine PU-Si polymer is deconvoluted into three components: the hydrocarbon peak at 284.8 eV (C–C and C–H bonds), the C2 component at 286.5 eV due to C–O bonds and the urethane peak (HN–C(=O)–O) at 288.5 eV. The latter peak can also appear due to COOH group contribution.²⁵ As result of the plasma treatment the shape of C1s peak changed significantly. It became larger and was decomposed into four components at 284.8, 286.5, 288.1, and 289.8 eV. First three peaks have the same assignments as in the pristine sample while the latter is probably due to the O–C=O bonds.²⁶ The plasma treatment results in decrease of the hydrocarbon component at 284.8 eV, while the peaks intensities at 286.5 and 288.1 eV increase. The relative area of all peaks is presented in the Figure 7 demonstrating that the concentration of the oxidized carbon species on the polymer surface increases after the plasma exposure. This finding is consistent with the enhanced polymer hydrophilicity after the plasma exposure. The energetic plasmas species mainly attack the weaker C–C and C–H bonds in the polymer chains. Then oxygen atoms are incorporated on the polymer surface introducing C–O and O–C=O polar groups, which leads to increase of the surface energy and reduction of the water contact angle.

For both samples, the treated and the untreated one, the O1s peak was resolved into two contributions with approximately same proportions: an intense contribution²⁵ at 532.5 eV due to C–O/N–COO and SiO₂ bonds and a weak peak (less than 10%) at 534.5 eV due to the carboxylic groups.⁷

The XPS spectra of the pristine PU-Si samples presented a single N1s peak at 400.2 eV due to the –N–COO bonds (urethane nitrogen). The N1s peak of DBD-treated polymer was decomposed into two components at 400.0 and 402.8 eV related to the –N–COO and N–O bonds, respectively.²³

The Si2p peak of the untreated PU-Si polymer was resolved into a single component at 102.4 eV corresponding to Si–O/Si–C bonds. After the treatment the Si2p peak was decomposed into two contributions at 102.6 eV and a peak at 103.9 eV associated with SiO₂. This result indicates that the siloxane

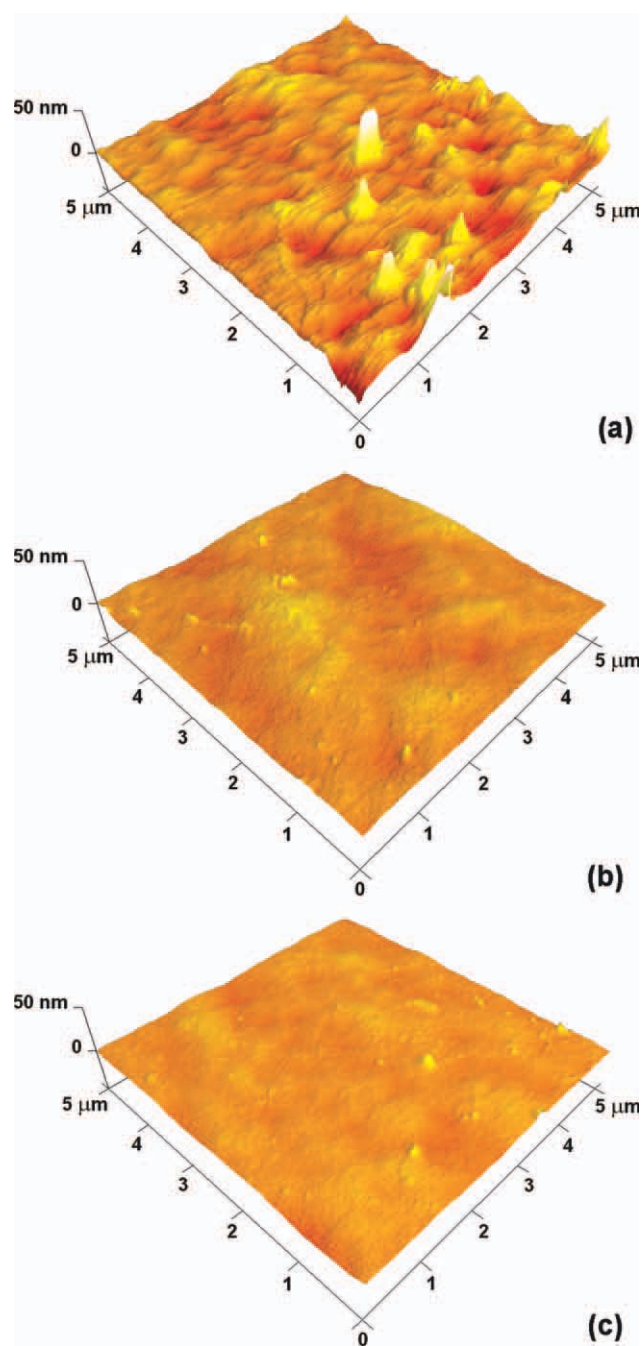


Figure 8 AFM images of PU-Si polymer: (a) pristine sample, (b) 5-min treated, and (c) 10-min treated sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

group was oxidized to complex silicates during the DBD treatment.

Another factor that influences the material wetting properties is the surface roughness. Bombardment of polymer surface by energetic particles such as electrons, ions, radicals and excited species causes removal of surface contaminants, amorphous materials, oxide layers, and adsorbed species resulting in surface etching. Surface morphology was evaluated

TABLE II
Comparison of PU Roughness Before and After the Plasma Exposure

	Pristine PU	5-min treated PU	10-min treated PU
Rms roughness (nm)	6.20	2.94	1.98

by AFM analysis. Figure 8 shows the 3D AFM images of the untreated and DBD treated polymers. The plasma exposure results in smoother surfaces, especially when longer treatment is applied.

The roughness values of the 5- and 10-min plasma-treated polymers as well as a pristine sample are summarized in Table II. As can be seen from this table the surface roughness of PU-Si polymers decreases as a result of plasma exposure. Similar reduction of polymer roughness was observed in low-pressure plasma treatments of PU^{7,14,25} and may be caused by selective etching of the urethane linkage.

Generally, the roughness of surfaces can enhance the mechanical interlocking thus altering the surface wettability of a sample.²⁷ However no influence on the contact angle was found if the surface roughness is below 0.1 μm .²⁸ The roughness of all samples presented in Table II is much smaller, so one can expect that in this case the surface morphology had no influence on the contact angle measurements. Therefore the enhanced surface wettability of plasma-treated PU-Si polymers can be correlated with the modified chemical composition of the surface due to the incorporation of O rather than surface structural modification.

CONCLUSIONS

The surface wettability of PU-Si polymer was modified by DBD in air. As evidenced by AFM and XPS analysis, the plasma exposure changes both the surface morphology and the surface chemical composition. The polymer surface became slightly smoother and oxygen atoms were incorporated onto the DBD-treated samples. However, the mild roughness reduction of the DBD-treated polymers probably does not affect the contact angle measurements. The air plasma treatment introduced oxygen-containing functional groups on the polymer surface. These surface chemical modifications resulted in a decrease of the water contact angle and enhancement of the surface energy of the DBD-treated polymers, converting their characteristics from hydrophobic to hydrophilic. However, the investigation of polymer aging behavior showed partial hydrophobic recovery of the polymer surfaces. This process is probably due to the reorientation of induced polar chemical

groups into the bulk of the material and the diffusion of unpolar groups from the subsurface layer to the surface. The increase of DBD treatment time led to more intense surface modification effect (surface oxygenation) resulting in polymer surfaces with smaller water contact angle that were less susceptible to hydrophobic recovery.

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