

# Improving hydrophobicity on polyurethane-based synthetic leather through plasma polymerization for easy care effect

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**Abstract** This study reports on the deposition of a hydrophobic coating on polyurethane (PU)-based synthetic leather through a plasma polymerization method and investigates the hydrophobic behavior of the plasma-coated substrate. The silicon compound of hexamethyldisiloxane (HMDSO), inactive gas argon (Ar), and toluene were used to impart surface hydrophobicity to a PU-based substrate. Surface hydrophobicity was analyzed by water contact angle measurements. Surface hydrophobicity was increased by deposition of compositions of 100% HMDSO, 3:1 HMDSO/toluene, and 1:1 HMDSO/toluene. Optimum conditions of 40 W, 30 s plasma treatment resulted in essentially the same initial contact angle results of approximately 100° for all three treatment compositions. The initial water contact angle for untreated material was about 73°. A water droplet took 1800 s to spread out on the plasma-treated sample after it had been placed on the sample surface. An increase in plasma power also led to a decrease in contact angle, which may be attributed to oxidization of HMDSO during plasma deposition. XPS analysis showed that plasma polymerization of HMDSO/toluene compositions led to a significant increase in atomic percentage of Si compound responsible for the hydrophobic

surface. The easy clean results for the treated and untreated PU-based synthetic leather samples clearly showed that the remaining stain on the plasma-polymerized sample was less than that of untreated sample. The plasma-formed coating was both hydrophobic and formed a physical barrier against water and stain.

**Keywords** Easy clean property, Hydrophobicity, PU-based synthetic leather, Plasma polymerization, HMDSO

## Introduction

Hydrophobic and super-hydrophobic surface treatments of different substrates have been of great interest in recent years for various applications, such as dust-free and self-cleaning surfaces for textiles, building applications, and corrosion protection.<sup>1–3</sup> Easy care properties are added to apparel including upholstery fabrics and garments that resist soiling and staining, by the application of chemicals.<sup>4</sup> Water/oil repellent finishes, including product groups such as metal salt paraffin dispersion, polysiloxane, and fluorocarbon polymers, provide hydrophobic properties to textiles. Polysiloxanes form a coating silicone film with methyl groups which is responsible for the hydrophobic properties of the finish.<sup>4</sup> In general, hydrophobic and super-hydrophobic surfaces have been produced either by creating a rough structure on a hydrophobic surface where the contact angle is higher than 90°, or modifying a rough surface by materials with low surface free energy.<sup>1,2,5</sup> In addition, the contact angles hysteresis becomes very low, producing a surface off which water droplets simply roll.<sup>5</sup> Conventionally, water repellence is accomplished by the use of solvents and organic reagents, mostly wax emulsions, quaternary ammonium salts, and hydrophobic resin finishes, which require discarding and can cause environmental

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problems because of the disposal of harmful waste in the treatment baths.<sup>6</sup>

Plasma polymerization is a unique technique used for modifying material surfaces by depositing a thin polymer film.<sup>7</sup> When polymeric materials are exposed to plasma, radicals are created in the polymeric chain. These radicals can initiate polymer reactions when they are in contact with monomers in a liquid or gaseous phase. Electrons in the plasma generate radicals at the surface of the polymeric material through excitation of the polymer molecules. As a result, a grafting polymer is formed on the surface of the polymeric material. The film so produced offers possibilities of anticorrosive surfaces, electrical resistors, scratch resistance coatings, optical filters, chemical barrier coatings, and water-repellency coatings.<sup>8,9</sup> In plasma processing, low quantities of reagents are used and little material needs to be disposed of due to the short treatment times, suggesting environmental advantages.<sup>7</sup> These films are pinhole-free and highly crosslinked and are therefore insoluble, thermally stable, chemically inert, and mechanically tough. Furthermore, such films are often highly coherent and adherent to a variety of substrates including conventional polymer, glass, and metal surfaces.<sup>10</sup> Due to these excellent properties, plasma-polymerized films can offer many practical applications in the field of mechanics, electronics, and optics.<sup>11</sup> Plasma polymerization at low pressure is already a well-established technology.<sup>12,13</sup>

Li et al. studied the plasma surface treatment of silk and cotton fabrics which was carried out in a hexafluoropropene ( $C_3F_6$ ) atmosphere under different experimental conditions, where water contact angles of  $122^\circ$  and  $127^\circ$  were reported on silk and cotton, respectively, originally having hydrophilic character.<sup>14</sup> Hodak et al. used radio-frequency inductively coupled  $SF_6$  gas plasma to modify the surface of Thai silk fabrics for the enhancement of the hydrophobic property. An increase in the water contact angle of fabrics from  $0^\circ$  up to  $145^\circ$  was observed after plasma treatment with  $SF_6$ .<sup>15</sup> Kamlangkla et al. studied the effect of radio-frequency inductively coupled  $SF_6$  plasma on the surface characteristics of cotton fabric where the water contact angle of  $149^\circ$  on the fabric surface was reported.<sup>16</sup>

Chemical modification of artificial materials to amplify the hydrophobicity and water repellency is traditionally achieved through addition of a coating material. It is known that water repellent coatings such as fluoro-polymers generate waste water and toxic dioxin.<sup>17,18</sup> However, surface modification through plasma polymerization of silicon compound is an environmentally friendly technology to improve the hydrophobicity due to nontoxic or of low toxicity, nonflammable or of low flammability characteristics of organosilicons which are inexpensive and commercially available.<sup>19</sup> Ji et al. reported the formation of water repellent film on PET fiber via plasma polymerization at atmospheric pressure. PET fiber was treated

by employing radio frequency (RF) plasma in a mixture of argon gas and gas-phase hexamethyldisiloxane (HMDSO). The sample passed 20 times through plasma treatment showed the water repellency rating of 90 based on the AATCC standard spray method.<sup>20</sup>

Although there have been a number of efforts to increase the hydrophobicity of textile-based substrates through plasma treatments,<sup>16–20</sup> little work has been done on plasma deposition on polyurethane (PU)-based synthetic leathers. In this study, a plasma polymerization method was used to reduce the surface wetting properties of PU-based synthetic leather. A water droplet placed on the surface of the treated samples took 30 min to spread, whereas spreading occurred within 15 min on the untreated samples. Plasma deposition resulted in the reduction of the wettability of the surface which was also evident from the improved stain release behavior of plasma-treated samples.

Plasma deposition of HMDSO/toluene at low pressure showed promising results at improving the surface hydrophobicity and easy clean property of PU-based synthetic leather. In the current study, a noncorrosive and nontoxic silicon compound of HMDSO was selected as the plasma coating material. An inert gas, argon (Ar), was used as the carrier for the monomer and an aromatic hydrocarbon, toluene, was used for reducing the surface polarity due to its nonpolar character.

This study aims at using the plasma processing as an ecological finishing method to improve the surface hydrophobicity and easy care property of PU-based synthetic leather which has been widely used in apparel, upholstery, and automotive applications.

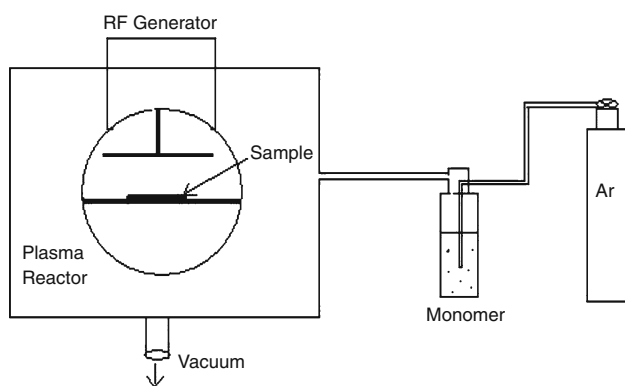
## Experimental

All experiments were carried out at 65% RH and  $21^\circ C$ .

In this work, HMDSO obtained from Aldrich (98% pure) was used as received. HMDSO was coated onto the textile substrate through a plasma polymerization method. Toluene was obtained from Aldrich (99.8% pure). PU-based synthetic leather samples manufactured for upholstery applications with a weight per unit area of  $556.7 \text{ g/m}^2$ , and thickness of 0.9 mm were supplied by a synthetic leather manufacturer (Flokser Tekstil San. Tic. A.S., Turkey). Argon was used as the carrier gas with a flow rate of  $1000 \text{ cm}^3/\text{min}$ . HMDSO was maintained at  $25^\circ C$ . It was bubbled by argon and injected to the plasma chamber.

### Plasma treatment

The schematic of the low pressure plasma system used for PU-based leather surface treatment is shown in Fig. 1. The system is a 13.56 MHz RF supply through an L-C matching unit with a maximum power of



**Fig. 1: Schematic of plasma system at low pressure used for coating of the textile material**

100 W. All of the samples in this work were treated at the plasma power of 20–100 W. Mixed HMDSO/toluene was injected through the reactor chamber, bubbled by 11pm argon gas. Treatments were carried out at a pressure of 40 Pa for 30–120 s. The experiments were performed varying the HMDSO/toluene mixing rate ratio. Compositions of 100% HMDSO and 3:1, 1:1 HMDSO/toluene were used during plasma polymerization on PU-based synthetic leather samples. Plasma polymerization was performed at different plasma power and plasma treatment time conditions in order to determine the conditions that provided the highest water contact angle and, therefore, the best hydrophobicity results. Samples without plasma treatment will be referred as “untreated” samples.

### Contact angle measurements

Water contact angles on PU-based synthetic leather samples before and after plasma polymerization of HMDSO and HMDSO/toluene mixtures were measured using a contact angle meter from KSV Instruments, Finland, equipped with CAM 200 software. Water contact angles were measured at different time intervals and the changes in water contact angles were observed and compared with those measured on an untreated sample. Distilled water droplets having a constant volume of 20  $\mu\text{l}$  were injected onto the sample surface using a syringe. The system was equipped with a CCD camera and a PC-based data processing and acquisition software. Droplet images were captured at a speed of 1 frames/s by the camera. The static water contact angles were measured automatically by the software using Young–Laplace curve fitting based on the captured droplet image profiles. Five different contact angle measurements were taken from each sample and measurements were repeated five times for one sample and then the average values were calculated. Contact angle measurements were taken on the samples right after the plasma treatment. Plasma power was varied from 20 to 100 W; plasma treatment times of 30, 60, 90, and 120 s

were applied during experiments. After the droplet was placed on the surface, water contact angles were taken at different time intervals from 0 to 180 s. In order to observe the lowest contact angle, a longer time scale was also used, i.e., 1800 s until the water droplet spread out on the plasma treated sample. Repeatability of contact angle measurements was achieved.

### Easy clean property

The easy clean properties for the untreated and plasma-treated PU-based synthetic leather were tested. A stain release test was performed using a standard hand-cranked reciprocating crock meter rubbing device (Taber Industries). The stained test sample was clamped to the instrument base and a square of standard plain white cloth was wetted with distilled water and fixed to the 16 mm diameter “finger” of the device. The “finger” rubbed against the sample with a pressure of 250 g force and traversed a straight path approximately 100 mm long with each stroke of the arm. In total, 20 strokes were applied during the test in order to compare stain removal from treated and untreated surfaces. Tests were repeated two times for each stain type, i.e., pen ink and mustard. Images of the remaining stain on the treated and untreated samples were taken for visual comparison.

### Scanning electron microscopy (SEM)

A Nova<sup>TM</sup> NanoSEM system from FEI was used for surface morphology characterization of the plasma-polymerized PU-based synthetic leather samples.

### X-ray photoelectron spectroscopy (XPS)

XPS analysis was performed to characterize the surface chemical composition of the plasma-polymerized PU-based synthetic leather samples. XPS measurements were conducted using a K-Alpha-monochromated high-performance XPS spectrometer system from Thermo Scientific, USA. The pressure in the analyzing chamber was maintained at  $10^{-7}$  Pa or lower during analysis and the size of the analyzed area was 7 mm  $\times$  7 mm. The binding energy value of 285.0 eV of the C1s core level was used as a calibration of the energy scale.

### Results and discussion

Different compositions of 100% HMDSO, 3:1 and 1:1 HMDSO/toluene were utilized during plasma polymerization experiments and the improvement in surface hydrophobicity obtained from different plasma depositions was compared.

**Table 1: Average water contact angle results of PU-based synthetic leather at different plasma conditions and HMDSO/toluene mixing compositions**

Plasma conditions		Mixture ratio								
Power (W)	Time (s)	3:1 HMDSO/toluene			1:1 HMDSO/toluene			100% HMDSO		
		Water contact angle (°)			Water contact angle (°)			Water contact angle (°)		
		t = 0 s	t = 90 s	t = 180 s	t = 0 s	t = 90 s	t = 180 s	t = 0 s	t = 90 s	t = 180 s
20	30	93.8 ± 2.8	78.1 ± 2.6	74.5 ± 3.0	100.4 ± 3.4	84.1 ± 3.3	78.8 ± 2.3	96.2 ± 3.1	81.2 ± 1.2	76.7 ± 1.6
	60	94.2 ± 2.1	80.2 ± 4.0	76.3 ± 2.2	94.7 ± 4.2	81.6 ± 3.0	77.6 ± 2.9	98.2 ± 2.8	85.3 ± 2.2	80.5 ± 1.9
	90	89.9 ± 1.7	76.2 ± 3.4	73.0 ± 3.9	90.2 ± 1.1	77.1 ± 2.6	74.3 ± 3.4	94.8 ± 2.8	81.3 ± 1.8	78.7 ± 2.2
40	120	88.2 ± 4.0	76.9 ± 3.3	71.3 ± 3.7	89.6 ± 2.3	78.1 ± 2.9	72.5 ± 2.2	93.3 ± 3.4	78.3 ± 2.1	74.3 ± 1.9
	30	99.7 ± 3.7	83.4 ± 3.2	79.2 ± 3.3	97.7 ± 0.9	85.0 ± 1.4	80.5 ± 0.4	95.6 ± 3.9	85.8 ± 3.2	77.7 ± 2.3
	60	88.3 ± 4.1	72.8 ± 3.9	69.3 ± 3.9	87.0 ± 1.4	71.0 ± 2.3	66.3 ± 2.4	85.8 ± 3.3	67.7 ± 2.3	66.7 ± 3.5
60	90	76.4 ± 2.2	57.0 ± 3.1	53.9 ± 3.6	75.3 ± 2.6	55.9 ± 2.4	52.8 ± 3.6	72.8 ± 2.9	54.1 ± 2.0	50.6 ± 1.3
	120	82.8 ± 3.1	61.6 ± 3.1	58.1 ± 2.8	81.9 ± 1.4	60.3 ± 3.9	56.9 ± 2.2	78.8 ± 3.4	57.7 ± 0.9	54.5 ± 1.2
	30	94.6 ± 3.4	81.9 ± 4.1	77.4 ± 0.4	91.6 ± 2.7	75.6 ± 3.3	71.0 ± 3.4	90.1 ± 3.3	74.6 ± 3.0	68.9 ± 3.8
80	60	85 ± 3.6	69.3 ± 2.2	66.6 ± 2.1	74.5 ± 3.6	58.5 ± 3.9	53.5 ± 3.6	74.8 ± 3.2	59.0 ± 3.5	54.5 ± 3.9
	90	79.5 ± 4.3	61.4 ± 2.6	56.9 ± 3.4	69.7 ± 3.9	51.0 ± 0.4	47.8 ± 0.8	69.3 ± 3.2	49.5 ± 2.5	46.9 ± 2.6
	120	75 ± 2.7	53.1 ± 3.4	49.8 ± 3.4	65.3 ± 4.1	44.1 ± 3.4	40.1 ± 2.7	66.5 ± 2.9	44.5 ± 1.7	39.7 ± 3.0
100	30	92.2 ± 4.2	76.1 ± 4.1	73.2 ± 4.0	97.6 ± 3.8	79.2 ± 3.0	72.7 ± 2.2	87.3 ± 3.9	71.1 ± 3.6	67.3 ± 2.0
	60	79.6 ± 3.8	61.8 ± 3.9	57.2 ± 2.2	82.1 ± 3.4	62.2 ± 3.9	57.6 ± 3.4	92.3 ± 4.1	76.9 ± 2.4	71.5 ± 2.9
	90	70.2 ± 4.6	52.0 ± 2.3	48.7 ± 2.5	67.2 ± 4.0	49.1 ± 2.3	45.8 ± 2.2	67.7 ± 3.3	51.6 ± 3.4	46.7 ± 2.6
100	120	68.3 ± 1.5	58.0 ± 1.8	41.1 ± 0.5	65.5 ± 3.5	54.9 ± 4.0	38.7 ± 2.1	66.7 ± 4.1	55.1 ± 3.5	39.0 ± 3.0
	30	89.7 ± 1.5	78.6 ± 0.7	69.2 ± 0.8	82.5 ± 3.7	73.3 ± 2.8	66.4 ± 1.0	79.8 ± 4.2	64.5 ± 3.3	60.1 ± 2.7
	60	75 ± 2.2	62.8 ± 2.8	51.5 ± 1.3	70.2 ± 3.3	59.1 ± 3.0	47.7 ± 1.9	61.5 ± 4.1	41.2 ± 2.9	36.2 ± 2.0
100	90	65.2 ± 1.1	54.1 ± 1.5	42.5 ± 1.3	60.4 ± 4.3	49.1 ± 3.1	37.5 ± 2.9	56.4 ± 2.2	46.2 ± 3.3	37.3 ± 2.6
	120	61.8 ± 1.4	47.4 ± 2.8	31.7 ± 1.2	56.8 ± 3.3	42.3 ± 4.0	26.7 ± 2.1	51.3 ± 2.8	39.6 ± 2.1	22.4 ± 1.7

### Water contact angle measurements

Average water contact angle results obtained from samples treated at different plasma conditions and using different HMDSO/toluene compositions are shown in Table 1. As the plasma treatment time was increased from 30 to 120 s, water contact angles decreased for all HMDSO/toluene mixing compositions. Overall the results showed that the highest contact angles were obtained at plasma power of 40 W and plasma treatment time of 30 s.

The water contact angles after plasma deposition (40 W, 30 s treatment) from 100% HMDSO, 3:1 HMDSO/toluene, and 1:1 HMDSO/toluene were essentially the same initially (approximately 100°) and all decreased by about 20° within 180 s, after the drop was placed on the surface. A decrease was expected due to water evaporation and drop retraction. A water droplet took 1800 s to completely spread out on the plasma treated sample after it was placed on the sample surface. The initial contact angle result for the untreated material was about 73°.

The water contact angle results showed that the surface hydrophobicity of PU-based leather samples was clearly improved after plasma polymerization of HMDSO/toluene on the material surface. This result may be attributed to the hydrophobic surface formed by silicon compounds with HMDSO/toluene plasma treatment.

Figure 2 shows the shapes and wetting behavior of water droplets deposited on untreated and plasma-polymerized PU-based synthetic leather samples at plasma power of 40 W and plasma treatment time of 30 s, for different HMDSO/toluene mixing compositions. The smaller size of the water droplets on the

untreated fabric is due to the water penetration through the pores on the surface of the substrate.

The contact angle results clearly indicated that plasma treatment enhanced hydrophobicity of PU-based synthetic leather. However, plasma polymerization results in a hydrophobic film coating at nano-scale. Since the thickness of deposited layer is relatively thin, it is difficult to obtain an even plasma coating on the synthetic leather substrate having an irregular surface morphology at macro-scale. Therefore, even after plasma treatment, the water contact angle changes and the water droplet spreads on the fabric surface depending on time. The movement of the droplet is controlled by surface properties, that is, surface energy and irregular surface morphology of synthetic leather. The difference in penetration behavior of water droplet on the untreated and plasma treated fabric is due to fact that plasma formed coating is as much a physical barrier as it is a hydrophobic layer.

Due to the hydrophobic layer deposited on the synthetic leather substrate, water droplets spread out and tended to stay on the plasma treated samples depending on time rather than penetrating into the structure. In order to observe the absorption behavior of water droplets, each of five synthetic leather samples was weighed precisely before 0.5 mL of distilled water was dispensed on each sample. Water droplets were left on the samples for 15 min. Following that, the liquid was removed from the substrate using absorbent paper. Then the samples were weighed again. The calculated weight gains of the substrates due to water absorption are provided in Table 2. Weight gain on the leather substrate due to droplet absorption was only about 1%, which showed that water droplet tended to

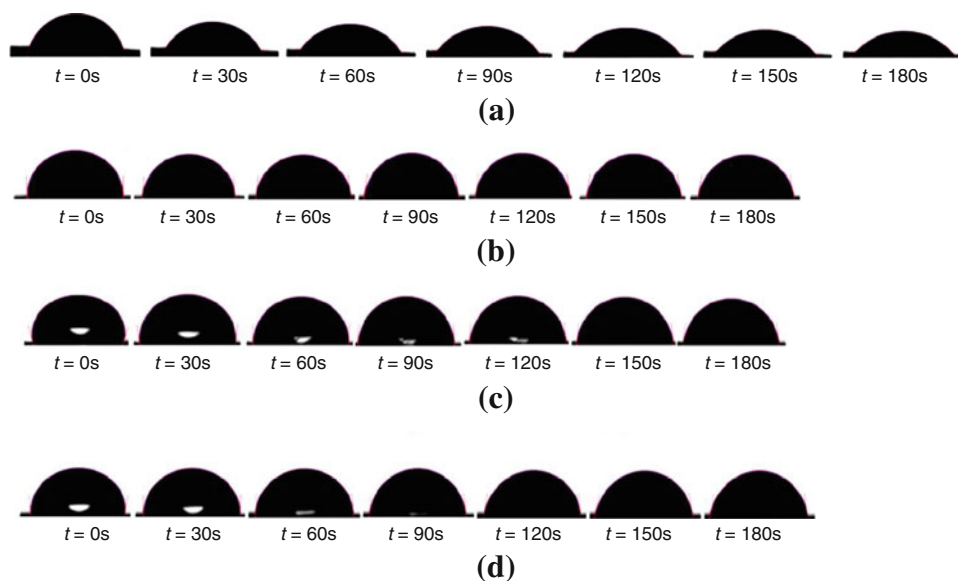
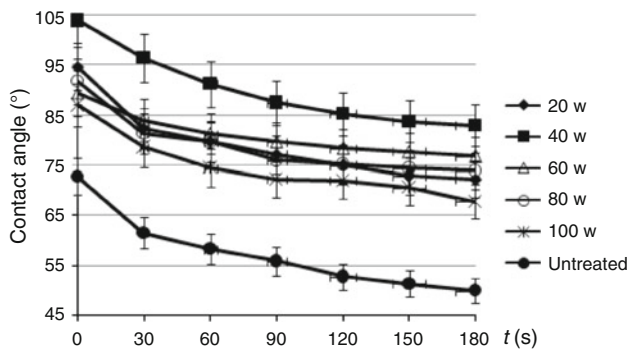


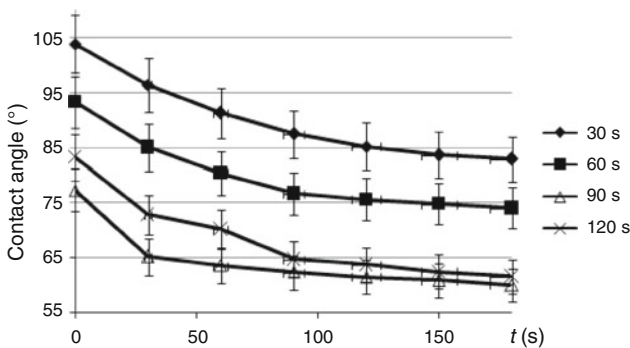
Fig. 2: Absorption of water droplet vs time,  $t$ , on (a) untreated, (b) 100% HMDSO, (c) 3:1 HMDSO/toluene, and (d) 1:1 HMDSO/toluene plasma-polymerized samples at plasma power of 40 W and plasma treatment time of 30 s

**Table 2: Weight gain of plasma-treated and untreated samples due to water absorption**

Sample	Average weight gain (%)
Treated	1.0203 ± 0.19118
Untreated	3.0468 ± 0.20103



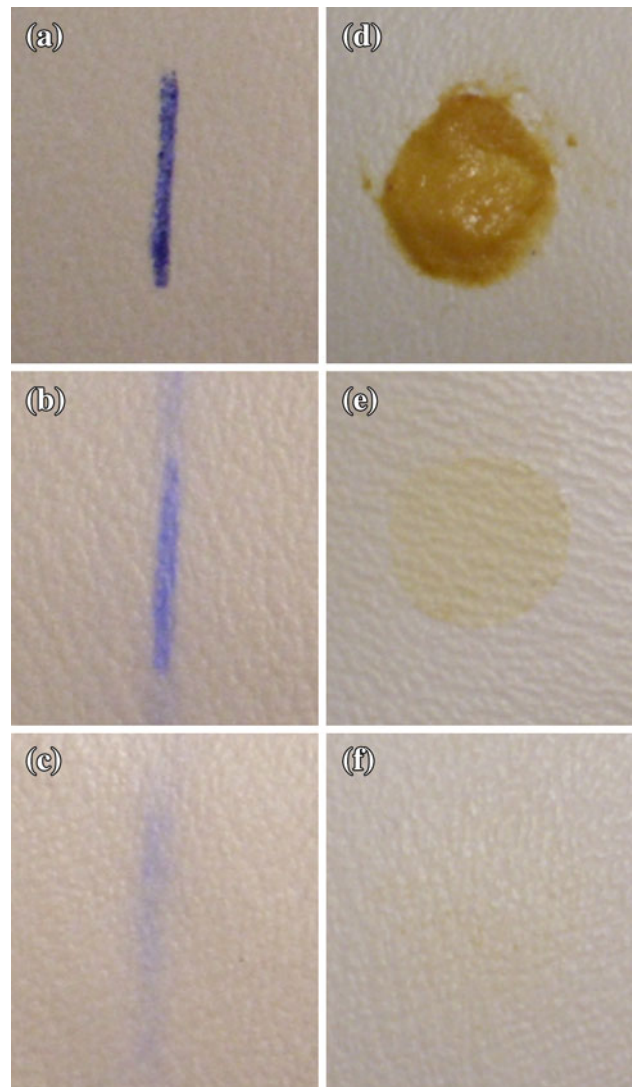
**Fig. 3: Contact angle vs time on plasma-polymerized PU-based synthetic leather sample with plasma treatment time of 30 s, using 3:1 HMDSO/toluene composition**



**Fig. 4: Contact angle vs time at different plasma treatment times from 30 to 120 s**

stay on the surface rather than penetrating into the structure. The lack of adsorption of water could be due or partly due to barrier properties of the plasma formed coating that had been produced. The hydrophobic coating acted as a barrier to keep out the water.

Figure 3 shows the water contact angle results by time on PU-based leather for an untreated sample and plasma-polymerized sample using 3:1 HMDSO/toluene with a plasma treatment time of 30 s, when plasma power was varied from 20 to 100 W. On the untreated sample surface, the water contact angle decreased from 70.8° to 49.1° within 180 s. Results showed that the increase in plasma power led to a decrease in contact angle indicating a decrease in surface hydrophobicity. As can be seen from Fig. 3, the most improved surface hydrophobicity was obtained at plasma power of 40 W. The silicon compound that coated the PU-based synthetic



**Fig. 5: Pen ink (a) and mustard (d) stains on the untreated samples. After 20 strokes of crock meter; the remaining pen ink stains on (b) untreated and (c) plasma-treated samples, the remaining mustard stains on (e) untreated and (f) plasma-treated samples**

leather through plasma polymerization showed the water repellency property.

Figure 4 shows the water contact angle results by time on PU-based leather at different plasma treatment times of 30 to 120 s. The plasma polymerization was performed using 3:1 HMDSO/toluene at a plasma power of 40 W. The highest water contact angle results were obtained at plasma treatment time of 30 s. The increase in plasma treatment time led to a decrease in water contact angles.

Figure 5 shows the stain removal results for the treated and untreated PU-based synthetic leather samples. After applying 20 strokes in the crock meter, the images clearly show that the remaining stain on the

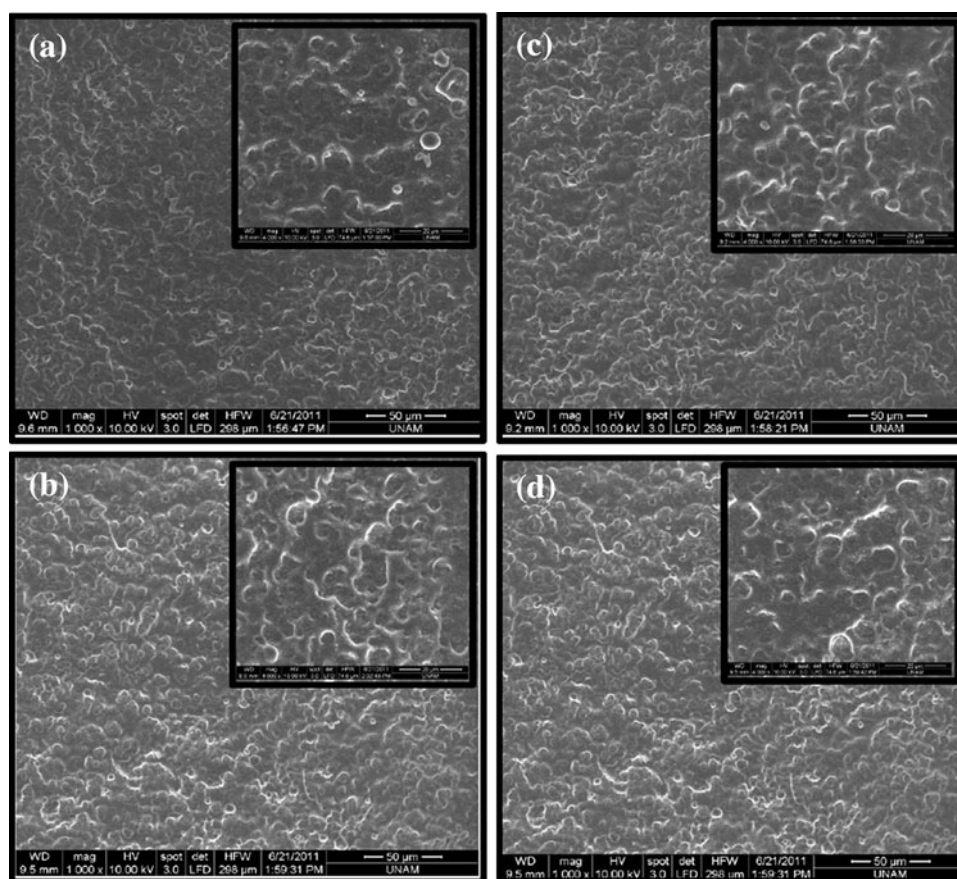


Fig. 6: The SEM images of (a) untreated, (b) 3:1 HMDSO/toluene, (c) 1:1 HMDSO/toluene, and (d) 100% HMDSO, at plasma treatment time of 30 s and plasma power of 40 W ( $\times 1000$ ), the inside images are of higher magnification ( $\times 4000$ )

Table 3: Elemental compositions of plasma deposited PU-based leather samples for different HMDSO/toluene compositions

Sample	Atomic percentages (%)				Peak binding energy (eV)				Atomic ratio	
	C	O	Si	N	C	O	Si	N	C/N	O/Si
Untreated sample	69.39	21.81	6.58	2.22	284.96	532.12	101.96	399.69	31.25	3.31
100% HMDSO 40 W 30 s	61.92	24.84	11.38	1.87	285.11	532.27	102.07	400.17	33.12	2.18
1:1 HMDSO/toluene 40 W 30 s	59.77	25	13.27	1.96	284.57	531.99	101.93	399.32	30.49	1.88
3:1 HMDSO/toluene 40 W 30 s	62.46	24.83	11.22	1.49	284.93	532.04	101.93	399.42	41.92	2.21
3:1 HMDSO/toluene 100 W 30 s	57.63	26.78	13.94	1.65	284.4	531.85	101.44	399.33	34.93	1.92

plasma-polymerized sample is less than that of untreated sample.

### Surface roughness

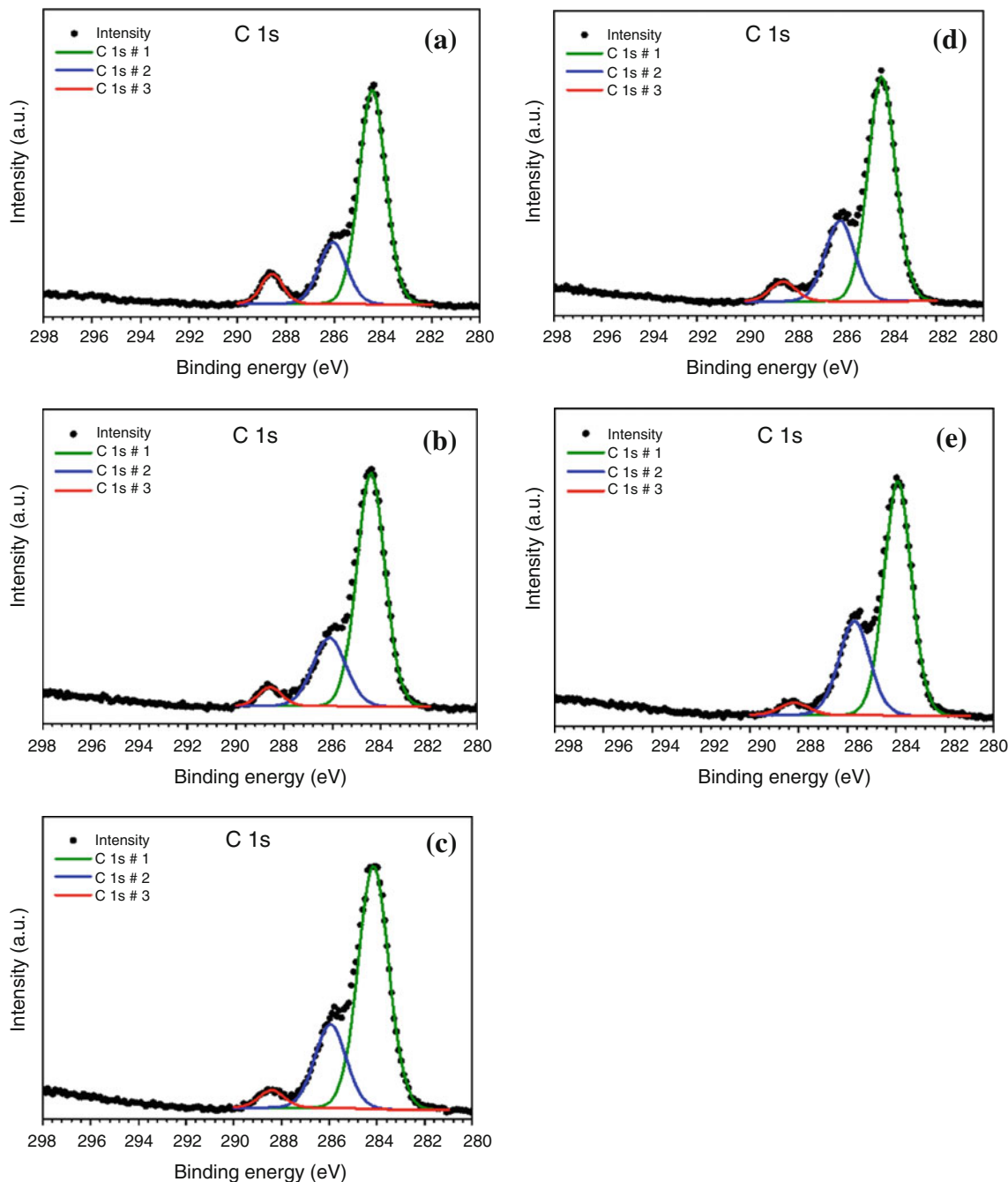
Figure 6 shows the scanning electron microscopy images of the PU-based synthetic leather sample

before and after plasma deposition of HMDSO/toluene mixing compositions. A slight change was observed in the surface roughness of the plasma-deposited material using HMDSO/toluene as compared to the untreated sample. The surfaces appear to have pores or pinholes which may be covered by the plasma-formed coating that would reduce the surface porosity.

**X-ray photoelectron spectroscopy (XPS)**

The surface chemistry of the untreated and plasma-deposited PU-based synthetic leather samples was studied by XPS analyses as summarized in Table 3. The main components of untreated and the plasma-deposited coating are carbon, oxygen, silicon, and a low percentage of nitrogen. The atomic ratio of C/N for different HMDSO/toluene compositions showed that

plasma polymerization led to a surface poorer in N belonging to PU and an atomic ratio of O/Si showed that plasma polymerization led to a surface richer in Si due to addition of silicon compounds with HMDSO/toluene plasma treatment. These atomic ratios showed that the highest amount of Si and the lowest amount of N were obtained with 3:1 HMDSO/toluene (40 W) plasma process, confirming the higher degree of plasma polymerization than with the other plasma processes. There



**Fig. 7:** Deconvoluted C1s peaks of (a) untreated PU-based leather sample, plasma-treated sample using (b) 100% HMDSO (40 W), (c) 1:1 HMDSO/toluene (40 W), (d) 3:1 HMDSO/toluene mixture (40 W), and (e) 3:1 HMDSO/toluene mixture (100 W)



**Table 4: Concentration of different silicon bonds in untreated and plasma deposited PU-based leather samples for different HMDSO/toluene compositions**

Sample	(CH <sub>3</sub> ) <sub>3</sub> SiO (101.5 eV)	CH <sub>3</sub> SiO <sub>3</sub> (102.8 eV)
Untreated sample	100	–
100% HMDSO (40 W)	92.59	7.41
1:1 HMDSO/toluene (40 W)	95.16	4.84
3:1 HMDSO/toluene (40 W)	94.6	5.4
3:1 HMDSO/toluene (100 W)	81.32	18.68

was 6.58% of silicon on the untreated sample which have come from the manufacturing of the synthetic leather. The presence of nitrogen on the sample surfaces after the plasma deposition of HMDSO monomer could be an indication that the monomer deposition with plasma process on the fabric was not uniform due to the nonuniform nature of the fabric or because the deposited layer was very thin. Moreover, the curve resolution of the C1s peaks for all samples was fitted with three peaks: one large peak at about 284.4 eV due to C–C or C–H bonds, the other peak at about 286 eV owing to –C–O and a small peak at approximately 288.57 eV due to N–C=O bonds from PU-based leather (Fig. 7). The percentage ratios of C–C/C–H peak to N–C=O peak showed that the N–C=O structure originated from PU-based leather decreased on the surface of the samples after plasma processes.

Table 4 also summarizes the concentration of different silicon bonds in untreated and plasma-deposited PU-based leather samples. The Si2p peak of the untreated sample has only one peak at about 101.5 which is attributed to (CH<sub>3</sub>)<sub>3</sub>SiO units.<sup>21</sup> However, the Si2p peaks of plasma-deposited PU-based leather samples are fitted with two peaks: one large peak at about 101.5 eV due to (CH<sub>3</sub>)<sub>3</sub>SiO units and a smaller peak at 102.8 eV which can be attributed to CH<sub>3</sub>SiO<sub>3</sub> units.<sup>21</sup> The reason for this result can be slight oxidation of HMDSO during plasma deposition under argon atmosphere.<sup>21</sup> According to the atomic percentages of silicon on the samples, the lower concentration of (CH<sub>3</sub>)<sub>3</sub>SiO<sub>3</sub> for 3:1 HMDSO/toluene plasma (40 W) treated sample indicated that less oxidation of HMDSO occurred during plasma deposition.

## Conclusion

We reported on the surface modification of PU-based synthetic leather substrates through plasma polymerization of different HMDSO/toluene mixture compositions. Wettability of the surface was reduced by the introduction of silicon atoms on the PU-based synthetic leather surface or formation of new silicon compounds layer through plasma deposition. Deposition of different

mixing compositions of 100% HMDSO, 3:1 HMDSO/toluene, and 1:1 HMDSO/toluene (40 W, 30 s treatment) resulted in essentially the same initial (approximately 100°) water contact angle on the plasma-treated samples. The plasma-formed coating was both hydrophobic and formed a physical barrier that kept out the water and improved the easy clean property of the synthetic leather.

Traditional methods such as wet processing, spray or direct coating have been used in the industry to apply hydrophobic chemicals such as fluorocarbon polymers, wax emulsions, hydrophobic resins, and metal salt paraffin dispersions, onto synthetic and natural leather products. These chemicals are applied onto the surface to provide protection from water, stains, and soil as well as to impart easy clean properties with minimal change in hand and color. The potential applications are garments, footwear, gloves, upholstery, and accessories.

Different from the traditional methods, deposition of a thin polymer film through plasma polymerization of HMDSO/toluene at low pressure showed a potential application as an ecological surface treatment method for easy care of PU-based synthetic leather. The method discussed in this study involves lower resource and energy consumption with the corresponding environmental damage compared to traditional wet chemical processes being used in the industry.

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