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Plasma Treatment for Preparing Durable Water Repellent and Anti-Stain Synthetic Fabrics for Automotive Applications

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Abstract

This paper describes the development of a plasma process to produce a durable water repellent and anti-stain thin film on synthetic textile, utilized for the upholstery in the automotive field. The coatings were deposited in non equilibrium low pressure plasmas fed with 1H, 1H, 2H-perfluo-ro-1-decene employing, as substrates, polyethylene terephthalate and polyethylene terephthalate thermo-coupled to polyurethane foam. It was found that the XPS F/C ratio of the deposit was higher than 1.4 and that the treated textile was always very hydrophobic (WCA > 140˚) and oil resistant (motor oil CA > 110˚), even after wear.

Keywords

Synthetic Textile, Automotive, Durable Water Repellent and Anti-Stain Character, Low Pressure Plasma, Fluorinated Coating

1. Introduction

The finishing processes of textiles devoted to improving the quality of the fabric and impart specific properties, such as hydrophobicity, hydrophilicity, anti-bacterical, flame retardant, shrink resistance, etc. [1]-[6], are becoming always and more important.

Both chemical and physical methods are generally used to obtain specific properties. The conventional treatments, including the widespread dip-coating and padding with chemicals, require the utilization of large amount

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of chemicals (generally in solution) with important environmental impact. These treatments may also affect the mechanical properties of the fabrics as, for instance, reducing the durability and the comfort to wear.

Alternative techniques have been investigated, during the last years, with the aim of reducing the utilization of chemicals. Among these, plasma treatment attracts particular interest especially for its main peculiarities: the treatments interest only the uppermost layers of the fabric surface without modifying the bulk properties [7] and it is environmental friendly, since the use of chemicals is negligible [8]. The utilization of low pressure plasma processes, in particular, has been widely investigated for the modification of surface properties of textile composed by synthetic polymers and natural materials [1] [2] [8]. The surface modifications and properties depend on the feeding gas and on the operating conditions (input power, pressure, electrode geometry, etc.); a proper selection of these parameters allows to obtain different processes with the same experimental apparatus, *i.e.* etching, grafting, cross-linking and deposition [2].

Despite these advantages, there are only few commercial applications of plasma treatments in the textile field, such as the employment of the process to increase the wettability of the fabrics up to 160 cm width developed in a plant build up from Niekmi Institute [9]. In addition to the difficult scale-up from lab to industrial scale, this could be due to the short lifetime of the plasma treatments that very often do not meet the demands of the textile industry in terms of resistance to washing, to light, to perspiration, etc. [2].

Among the different textile properties that can be improved with the plasma technology, the water repellency and the resistance to motor oil stains are very important for automotive applications. Several research groups investigated the hydrophobicity enhancement of polymers and fabrics using plasmas fed with fluorocompounds, e.g. tetrafluoromethane (CF_4) [10], sulphur exafluoride (SF_6) [11], exafluoroethane (C_2F_6) [12], exafluoropropene (C_3F_6) [13], etc. It was found that plasma fed with small molecules (e.g. CF_4, C_2F_6) did not result in treatments of good durability, probably for the formation of short polymer segments dangling on the treated surface [11]. For example, a coating with F/C ratio of 1.04 deposited on silk and cotton in plasma fed with C_3F_6 shows a good hydrophobic character (water contact angle, WCA higher than 120˚), but suffers a partial loss after water-washing and alcohol-extraction.

In this paper, the plasma enhanced-chemical vapor deposition (PE-CVD) with a large fluorinated molecule, the 1H, 1H, 2H-perfluoro-1-decene, is studied in order to impart to the synthetic textile, employed for vehicle interiors in the automotive industry, durable water repellency and anti-stain character respect to motor oil.

It was found that when a 100 nm thick layer with a surface XPS (X-ray photoelectron spectroscopy) F/C ratio higher than 1.4 is deposited, the treated textile is very resistant to water (WCA~150˚) and oil (motor oil contact angle, CA~120˚). These properties are preserved also after usury caused by a test which simulates the wear suffered by a car seat during its use for the average lifetime of the vehicle.

2. Materials and Methods

2.1. Low Pressure Plasma Treatment Experimental Conditions

Treatments were performed on as received substrates (80 × 80 mm) made of polyethylene terephthalate (PET) and of polyethylene terephthalate thermo-coupled to 5 mm tick polyurethane (PU) foam. These materials are commonly used by the automotive industry for the production of car and commercial vehicles interiors.

The experiments were carried out in the stainless steel, parallel plate, low pressure reactor depicted in **Figure 1**.

It consists of a cylindrical stainless steel chamber (internal diameter = 200 mm; height: 400 mm) equipped with two stainless steel circular electrodes (diameter = 150 mm, inter-electrode distance = 40 mm), pumped by a turbomolecular-rotary pumping system. The pressure was measured and controlled with a baratron gauge (MKS) and a manual throttle valve, respectively. The upper electrode was connected to a 13.56 MHz radio frequency (RF) power supply though an automatic L-type matching network unit, while, the lower electrode, on which the textile samples were positioned during the deposition processes, was grounded.

The experiments were performed at 2.0 Pa and 10 - 100 W of input power, with the flow rate of 1H, 1H, 2H-perfluoro-1-decene vapour (*Sigma Aldrich*, purity > 99.9%) fixed, through a needle valve, at 15 sccm (standard cubic centimeters for minute).

2.2. Surface Characterization of Plasma Modified Textiles

The thickness of the coating was determined by means of a KLA *Tencor* D120 profilometer on Si-c (100) sub-

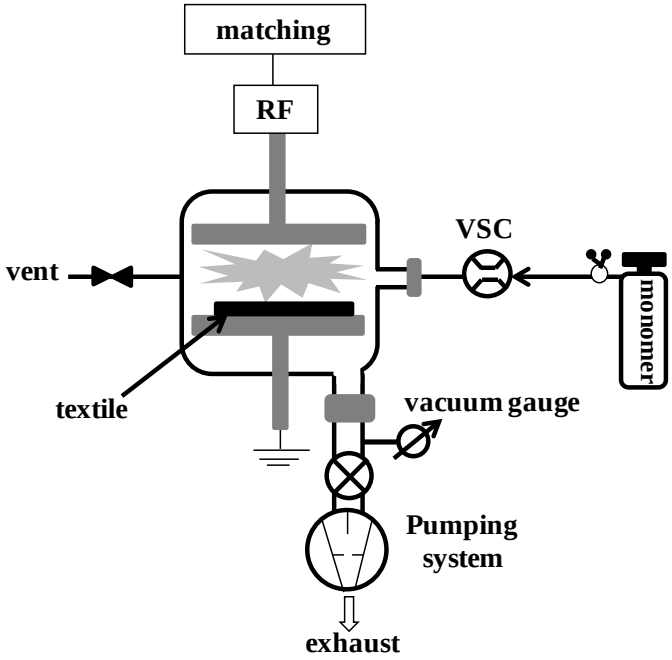


Figure 1. Schematic of the low pressure plasma reactor.

strates (flat reference material), partially masked during the deposition process.

The chemical characterization of treated and untreated samples was performed by means of X-ray Photoelectron Spectroscopy, using a Theta Probe spectrometer (*Thermo Electron Corporation*) equipped with monochromatic Al Kα X-ray source (1486.6 eV), operated at a spot size of 300 μm corresponding to a power of 70 W. Survey (0 - 1200 eV) and high resolution spectra were recorded in FAT (fixed analyzer transmission) mode at a pass energy of 200 and 100 eV, respectively. All spectra were acquired at a takeoff angle of 37˚. A flood gun was used to balance surface charging. The C1s signal for the hydrocarbon component (285.0 eV) was used as internal standard for charging correction. Atomic percentages were calculated from the high resolution spectra using the Scofield sensitivity factors set in the XPS data processing software and a non-linear Shirley background subtraction algorithm. Repeated measurements allowed registering a maximum relative standard deviation of about 3%.

Surface morphology of treated and untreated textile was evaluated using a *Zeiss* SUPRA™ 40 field emission scanning electron microscope (FESEM). Images were acquired after chrome metallization at a tilt angle of 0˚ at an acceleration voltage of 2 KV.

The water and oil wettability of textile samples was studied by static and/or dynamic water and motor oil (*Red Line synthetic oil*, 5w40) contact angle measurements, performed by means of an automatic goniometer (*Nordtest*), utilizing droplets of 2 μl of volume. The contact angle values were obtained averaging three measurements conducted in different parts of the same sample and on three different samples.

The wear resistance of treated and untreated surfaces was evaluated with a "Cesconi" abrasion tester, according to UNITEX 7858 rule, which reproduces the mechanical stress suffered by a car seat during its normal use for the average lifetime of the vehicle.

The test was carried out employing an abrasimeter general utilized for texting textile, leather, imitation leather (PU; polyvinyl chloride, PVC), non-woven, ceramic, rubber, etc. The abrading unit was made of PET textile fixed on a rotating plate. The substrate to test was located on a rotating "satellite" situated under the rotating plate, as schematized in **Figure 2**.

The "satellite" and the rotating plate rotated with different speeds, in order to ensure a uniform ablation of the analyzed sample.

A wear cycle of 3000 revolutions was performed with a load of 1 Kg, according to the internal FIAT validation test. Three different samples for each condition were examined.

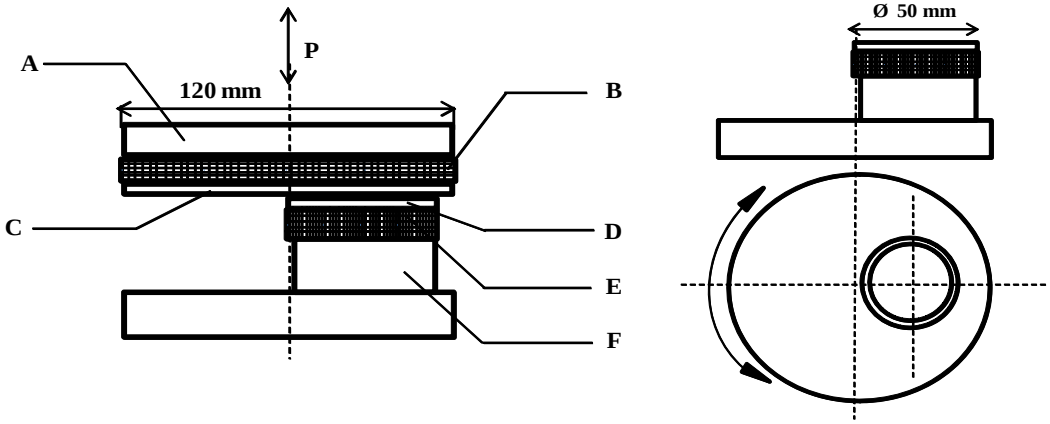


Figure 2. Scheme of the wear resistance test device. The substrate to test (D) is mounted on the satellite (F) through a substrate holder (E), while the abrading fabric (C) is fixed on the rotating plate (A) employing the substrate holder (B), on which the weight (P) is applied.

3. Results and Discussion

The XPS atomic composition and the F/C ratio of the plasma treated uncoupled PET are reported in **Table 1**, as a function of the input power. The chemical composition of virgin PET is also quoted for comparison.

Under the deposition conditions utilized, the effect of input power on the surface composition of the fluoropolymer coatings is very low. The F/C ratio varies in a narrow range (*i.e.* 1.47 - 1.65), the highest value is obtained at the lowest input power (20 W), probably for the light plasma fragmentation which preserves the chemical integrity of the monomer. The low effect of input power on the chemical composition of the coatings is reflected also on their hydrophobic/oleophobic behavior. As it can be appreciated in **Figure 3**, in fact, all samples have similar oil and water contact angles, with a slight reduction by increasing the input power (*i.e.* decrease of the fluorine content).

Untreated textile, on the other hand, was super-hydrophilic and super-oleophilic, in fact, contact angle measurements were not possible, because the drops of water and oil were instantaneously adsorbed by the sample.

SEM observations showed that all plasma coatings were compact and uniformly covered the fabric.

In order to evaluate the utilization of the optimized plasma treatment to produce water repellent and anti-stain fabric for seat upholstery in automotive field, the experiments were repeated under the same conditions on thermo-coupled PET textile. No difference, respect to the uncoupled substrate, was detected for the water and motor oil contact angle values. This is an important result because it means that the plasma treatment can be performed after the thermo-coupling process between the PET fabric and the polyurethane foam. Since the plasma treatment in part interests also the back side of the fabric, whether the treatment was carried out before the thermo-coupling step, it would result in pour textile-foam adhesion.

The wear resistance of the plasma coated thermo-coupled fabrics was evaluated with the "Cesconi" test described in the section "Materials and Methods". **Figure 4** reports the static contact angles of water and oil, measured after the wear test. All values were collected after 120 seconds of contact of the water/oil drop on the textile surface.

All the samples preserved the hydrophobic character after the test even though, by the comparison with **Figure 3**, it appears that, except for the sample treated at 100 W, the WCA values decrease after the wear test. Also the static motor oil CA values decrease after the wear test; the lowest reduction is shown by the sample treated at highest input power value (100 W).

Figure 5 clearly shows that the samples with the coatings deposited at 50 and 100 W exhibit a good and stable oleophobic character, also after the wear test. On the contrary, the fabrics coated at 20 and 30 W, despite their initial super-hydrophobic/oleophobic behavior, after the wear test became oleophylic.

The loss of the hydrophobic and oleophobic character suffered by the plasma modified fabrics can be due to mechanical damage caused by the "Cesconi" test. This damage is lower for the coatings deposited at 50 and 100 W, probably for the higher cross-linking promoted by the high input power which results in higher precursor

fragmentation and stronger ion bombardment. This is confirmed by the SEM images acquired after the wear test (**Figure 6**), that clearly show as the coating deposited at 100 W does not suffer serious mechanical damages, while the coating deposited at 20 W is almost completely destroyed after wear test. Also XPS analyses are in agreement with this conclusion, in fact, while the surface chemical composition of the coating deposited at 100 W shows small changes after the wear test (e.g. the fluorine content decreases from 58% to 51%), the XPS surface

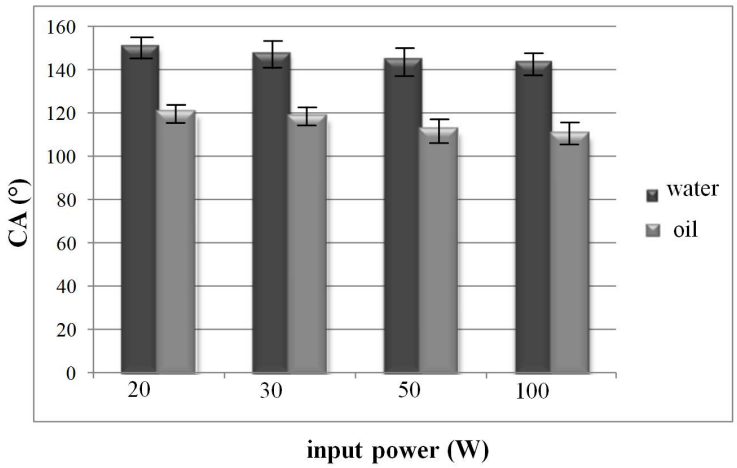


Figure 3. Water and oil contact angle values for plasma coated uncoupled PET textile vs. input power.

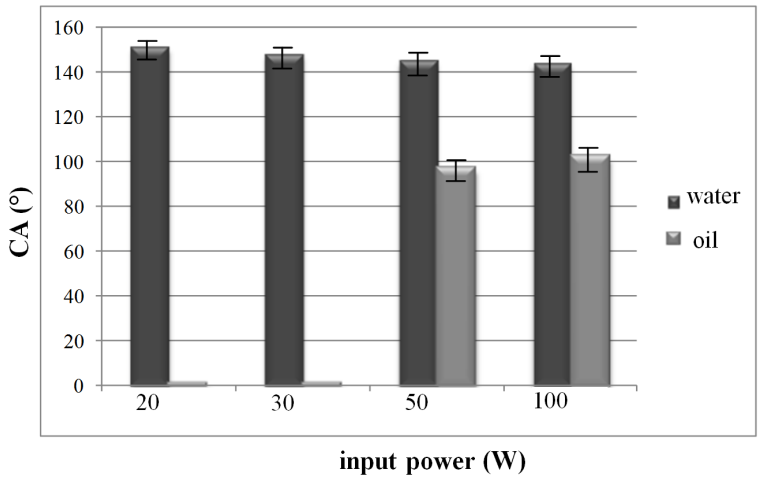


Figure 4. WCA and motor oil contact angle values measured after 120 seconds of contact of the worn thermo-coupled textile with the drop. The oil contact angle for the samples treated at 20 W and 30 W was zero.

Table 1. XPS results of uncoupled PET textile, as a function of input power (coating thickness, 100 nm).

Input Power	C %	O %	F %	F/C
Virgin Textile	74 ± 1	26 ± 2	/	/
20 W	37 ± 3	2 ± 1	61 ± 3	1.65
30 W	38.0 ± 0.7	3.1 ± 0.5	58.9 ± 0.6	1.55
50 W	39 ± 2	2.1 ± 0.4	58.9 ± 0.5	1.51
100 W	39.5 ± 0.5	2.5 ± 0.5	58 ± 2	1.47

chemical composition of the coating deposited at 20 W varies considerably after the wear test (e.g. the fluorine content decreases from 61% to 13.7%).

These experimental evidences allow to conclude that PET textile, thermo coupled with PU foam and coated with 100 nm of a fluorinated thin film deposited in low pressure plasma at 100 W, can be considered as possible, durable, water repellent and anti-stain material for automotive uses.

4. Conclusions

In this paper, a durable water/motor oil resistant fluorinated coating (F/C ≥ 1.47) was deposited in low pressure plasma conditions. The optimized film was used to cover the thermo coupled with 5 mm of polyurethane foam synthetic textile, generally used in automotive field. The obtained fabrics were wear resistant, particularly if they

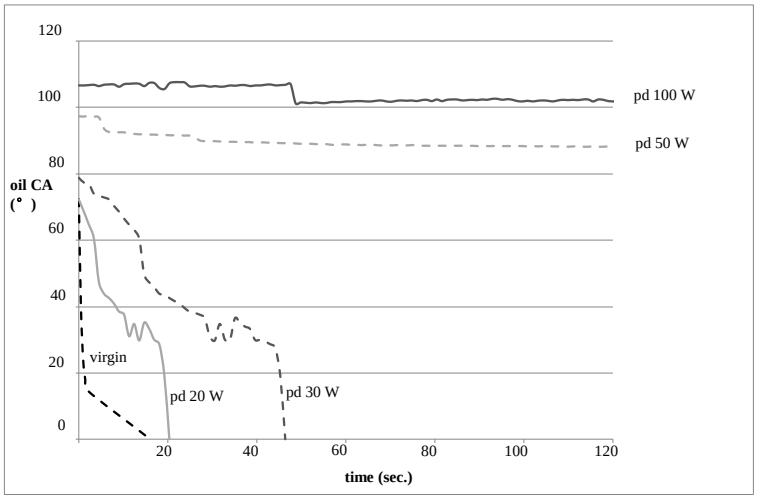
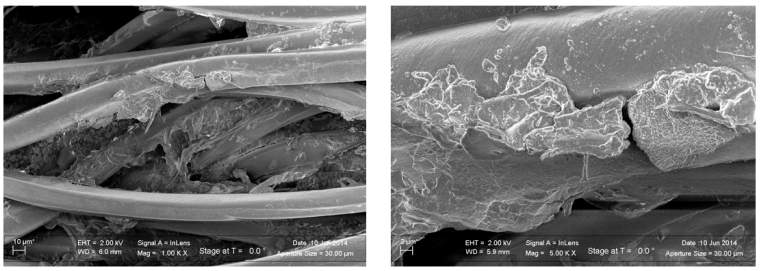
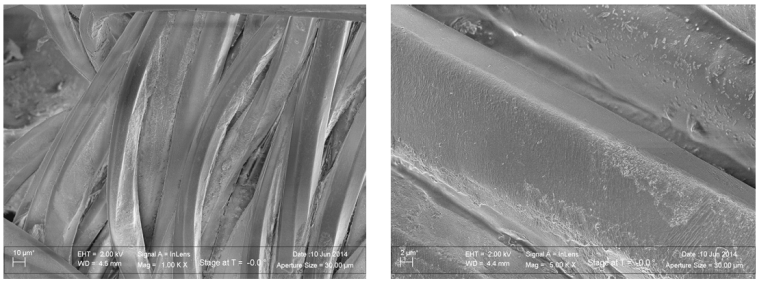


Figure 5. Dynamic motor oil contact angle values after "Cesconi" test for plasma coated thermo-coupled textile.



(a)



(b)

Figure 6. SEM images (magnification 1 and 5 Kx) of PET textile, thermo coupled with 5 mm of PU foam, coated with plasma coatings after "Cesconi" test. Plasma coating obtained at 20 W (a) and 100 W (b) of input power value.

were modified at high value of input power.

The optimized deposition process can be potentially employed in automotive field to obtain durable, water repellent and anti-stain textiles useful for the realization of car and commercial vehicle interiors.

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