

# Supplementary Materials

Fluorine-free plasma polymers to obtain water-repellent cotton fabrics: how to control their durability?

*Syrine Jebali, Jamerson Carneiro de Oliveira, Aissam Airoudj, Asma Riahi, Philippe Fioux, Fabrice Morlet-Savary, Ludovic Josien, Isabelle Ferreira, Vincent Roucoules, Florence Bally-Le Gall*

## **Additional information on Methods - Characterization of HMDSO plasma polymer thin films**

### **S1.1 Attenuated Total Reflection Fourier Transform Infrared spectroscopy (ATR FTIR)**

ATR FTIR spectroscopy was used to analyze the chemical composition of HMDSO plasma polymers. Measurements were performed on an FTIR spectrometer iS50 equipped with a highly sensitive, low-noise, MCT detector and coupled with a grazing angle Germanium ATR accessory (VariGATR). The angle of incidence was 65°. Spectra were collected at wavenumbers ranging from 650 to 4000 cm<sup>-1</sup>, with a resolution of 4 cm<sup>-1</sup> and a total of 64 scans. A minimum of three spectra were recorded for each sample.

### **S1.2 X-ray Photoelectron Spectroscopy (XPS)**

XPS analyses have been performed to determine the outermost surface chemistry of the deposited films using a VG SCIENTA SES-2002 spectrometer equipped with a concentric hemispherical analyzer. The incident radiation used was generated by a monochromatic Al K $\alpha$  X-ray source (1486.6 eV) operating at 420 W. Emitted photoelectrons were collected at a take-off angle of 90° from the substrate with electron detection in constant analyzer energy mode. The survey spectrum was recorded with a pass energy of 500 eV and a step size of 0.5 eV whereas for high-resolution spectra pass energy was set to 100 eV with a step size of 0.1 eV, selecting a spot size of approximately 4 x 6 mm<sup>2</sup>. Peak fitting was carried out with mixed Gaussian-Lorentzian (30%) components with equal full-width-at-half-maximum (fwhm) values using CASAXPS software (version 2.3.18). The surface composition expressed in at.% was determined using integrated peak areas of each component and took into account the transmission factor of the spectrometer, mean free path, and Scofield sensitivity factors of each atom (C1s: 1.00, O1s: 2.93 and Si2p: 0.95). For the deconvolution of the Si2p core levels, the maximum of the C1s peak, fixed at 284.38 eV and corresponding to carbon bonded to silicon, was used as a reference. The validity of this reference was confirmed by the position of the O1s peak at 532.0 eV. The Si2p peak was fitted with four Si2p components of equal fwhm with the following constraints as for the position of the peaks: T (102.75-102.9 eV), D (101.8-102.1 eV), M (100.8-101.5 eV) and Z (99.7-100.3 eV). Intensities were left free to fit. It can be noted that it was systematically verified that no additional component (named Q) at approx. 103.6 eV, corresponding to a silicon atom surrounded by four atoms of oxygen, was required to fit the experimental data.

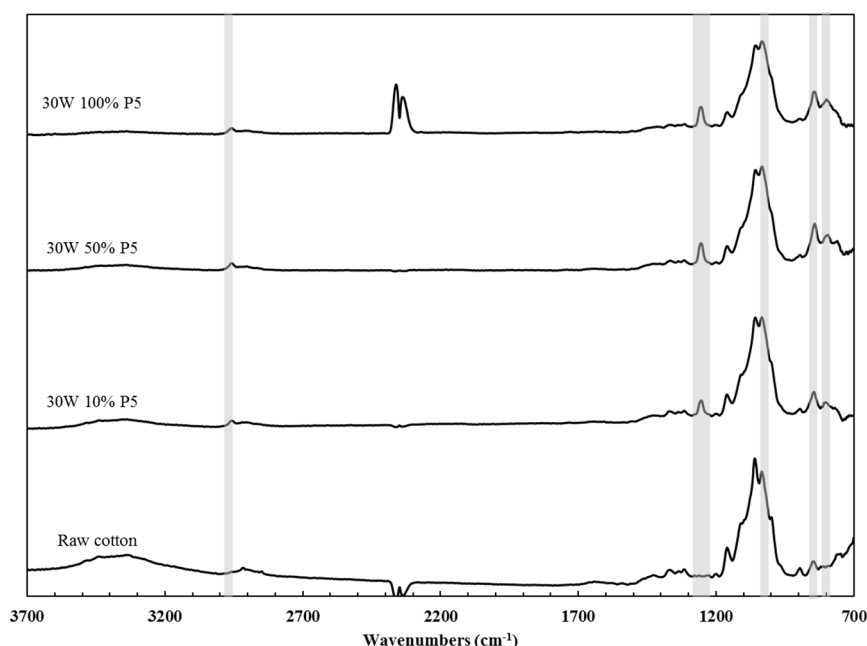
### S1.3 Ellipsometry

The coatings thicknesses were estimated on silicon wafers by ellipsometric spectroscopy. The measurements were performed on a UVISEL ellipsometer from Horiba–Jobin–Yvon (spectral range 190–830 nm). Data were fitted with the software from the UVISEL ellipsometer using a Tauc-Lorentz model. The average thickness value was estimated using at least five measurements made at different positions of the sample.

### S1.4 Water shedding angle measurements

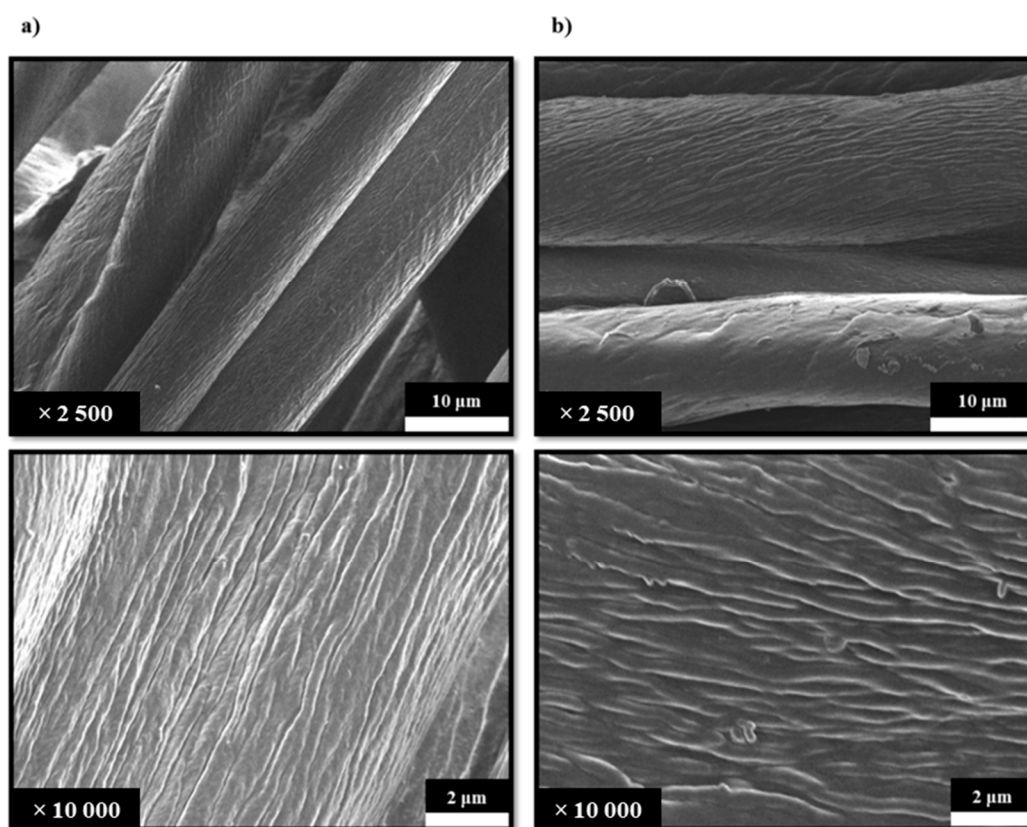
The water shedding angle ( $\Theta$ SHA) has been determined with the same equipment. In fact, for rough substrates, the measurement of the so-called shedding angle enables one to get an idea about the sticky or slippery behavior of the surface. Developed by Zimmermann et al., this method consists of releasing a droplet of the probe liquid onto the substrate from a defined height. The minimum angle of inclination at which the substrate needs to be tilted to ensure that all droplets completely bounce or roll-off the substrate corresponds to the shedding angle.[1] The tilting angle of (treated) cotton samples was firstly fixed at  $45^\circ$  and five droplets of  $10\ \mu\text{l}$  of distilled water were released from a distance of 10 mm above the surface of the samples (at five different positions). If all droplets completely bounced or rolled down, the tilting angle was successively decreased by  $2^\circ$  for  $\Theta\text{SHA} > 15^\circ$  or  $1^\circ$  for  $\Theta\text{SHA} \leq 15^\circ$  until at least one droplet was unable to slide off the surface. The average values of water shedding angles were then obtained from five different samples prepared in similar conditions but during different plasma polymerization experiments.

### Presence of plasma polymer coatings (synthesized with HMDSO) on cotton fabrics (before washing)



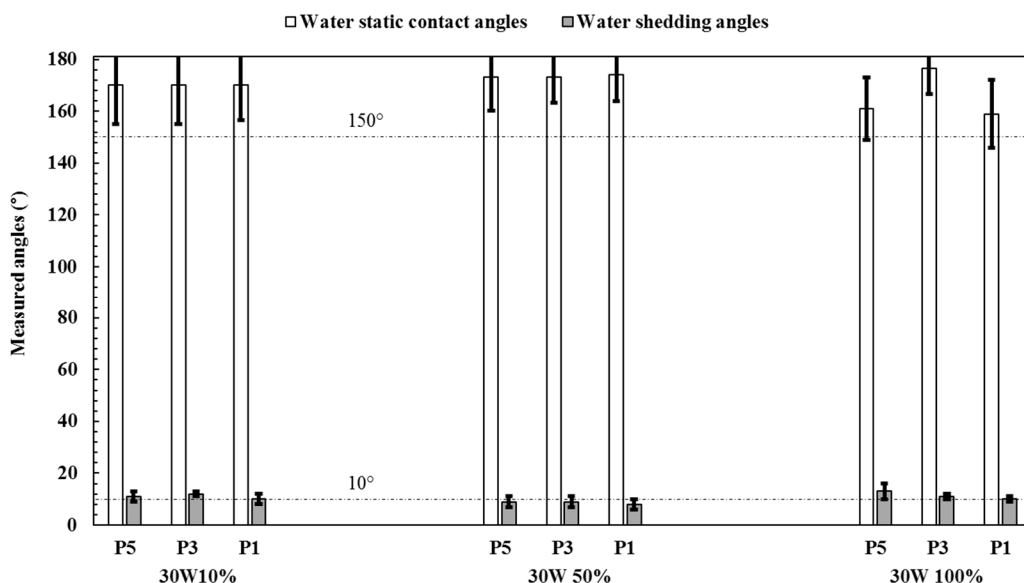
**Figure S1.** ATR-FTIR spectra of untreated cotton fabrics and treated ones with HMDSO plasma polymers deposited at different duty cycles (solely spectra obtained at position P5 are shown but similar tendencies have been observed for other positions). Wavelength ranges corresponding to positions of characteristic bands of HMDSO plasma polymers have been highlighted in gray to facilitate the reading.

The spectrum of untreated cotton reveals the typical chemical fingerprint of untreated cellulose. The bands at  $990\text{ cm}^{-1}$ ,  $1030\text{ cm}^{-1}$ ,  $1057\text{ cm}^{-1}$ ,  $1107\text{ cm}^{-1}$ ,  $1160\text{ cm}^{-1}$ ,  $1316\text{ cm}^{-1}$ ,  $1338\text{ cm}^{-1}$  and  $1372\text{ cm}^{-1}$  can be assigned to C–O stretching (two bands), asymmetric in-plane ring stretching, asymmetric C–O–C bridge stretching (two bands), CH wagging, OH in-plane bending and CH bending vibrations, respectively. Other bands such as OH stretching in the range  $3550\text{--}3100\text{ cm}^{-1}$  and CH stretching in the range  $2980\text{--}2800\text{ cm}^{-1}$  can be identified.[2] The ATR spectra of all cotton fabrics coated with HMDSO plasma polymer show distinct bands at  $2960\text{ cm}^{-1}$ ,  $1260\text{ cm}^{-1}$ ,  $840\text{ cm}^{-1}$  and  $800\text{ cm}^{-1}$ . The occurrence of these bands can be attributed to the presence of HMDSO plasma polymer corresponding to  $\text{CH}_x$  asymmetric stretching,  $\text{CH}_3$  bending vibrations in  $\text{Si}-(\text{CH}_3)_x$  and  $\text{CH}_3$  rocking vibrations in  $\text{Si}-(\text{CH}_3)_3$  and  $\text{Si}-(\text{CH}_3)_2$ , respectively. The band at  $1040\text{ cm}^{-1}$  corresponding to Si–O–Si asymmetric stretching vibrations is more difficult to exploit since it overlaps characteristic vibration bands coming from cotton. The careful analysis of these spectra enables to conclude that HMDSO plasma polymers have been deposited on cotton fabrics whatever the plasma polymerization conditions were. However, no quantification was possible due to the important overlapping of signal coming from the cotton in the  $1000\text{--}1100\text{ cm}^{-1}$  wavelength range.



**Figure S2.** SEM images at different magnifications of cotton textile fabrics before (a) and after (b) plasma polymerization of HMDSO (DC = 50%, P5).

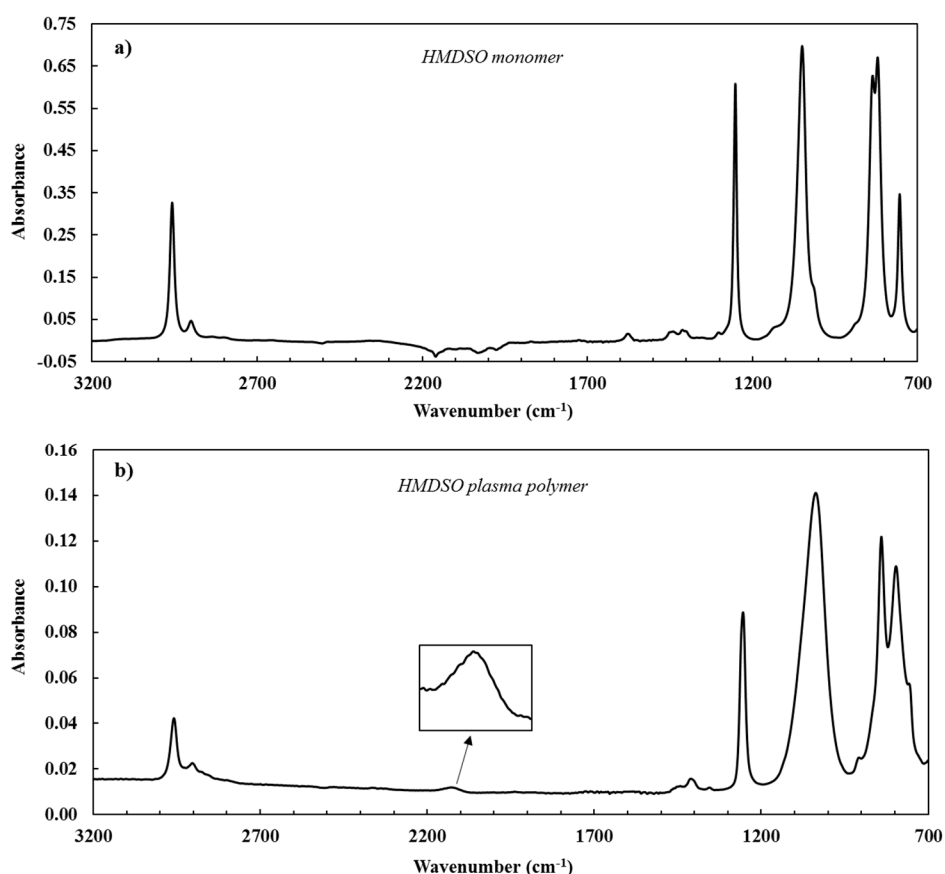
## **Evaluation of the superhydrophobic behavior of cotton fabrics after the plasma polymerization of HMDSO**



**Figure S3.** Water static contact angles and water shedding angles measured on HMDSO plasma polymers deposited on cotton fabrics in different conditions.

## **Chemical characterizations of HMDSO plasma polymers deposited on Si wafer**

Chemical surface characterizations by ATR-FTIR spectroscopy have been performed on samples prepared at different DC (10 to 100%) and different reactor positions (from P1 to P5). In accordance with the literature, [3–5] the main vibration bands from the monomer are conserved in the polymer spectrum: the  $\text{CH}_x$  ( $x = 1, 2, 3$ ) symmetric and asymmetric stretching vibrations at  $2900\text{--}2960\text{ cm}^{-1}$ , the  $\text{CH}_3$  bending vibrations in  $\text{Si}-(\text{CH}_3)_x$  at  $1260\text{ cm}^{-1}$ , the  $\text{CH}_3$  rocking vibrations in  $\text{Si}-(\text{CH}_3)_3$  at  $840\text{ cm}^{-1}$ , the  $\text{Si}-\text{C}$  symmetric stretching vibrations at  $760\text{ cm}^{-1}$  and the most intense peak located close to  $1040\text{ cm}^{-1}$ , which is attributed to the  $\text{Si}-\text{O}-\text{Si}$  asymmetric stretching vibrations (see Figure S4). Compared to the spectrum of the monomer, the  $\text{Si}-\text{O}-\text{Si}$  band in the spectrum of the polymer is broader and slightly shifted to lower wavenumbers (from  $1050\text{ cm}^{-1}$  to around  $1040\text{ cm}^{-1}$ ). This result indicates a structural change in molecules containing  $\text{Si}-\text{O}-\text{Si}$  chemical groups, which can be assigned to an increase in molecular weight after polymerization. In addition, the vibration band corresponding to  $\text{CH}_3$  rocking in  $\text{Si}-(\text{CH}_3)_3$  at  $840\text{ cm}^{-1}$  is split into two bands at  $840\text{ cm}^{-1}$  and  $800\text{ cm}^{-1}$ , the latter being assigned to  $\text{CH}_3$  rocking in  $\text{Si}-(\text{CH}_3)_2$ . The presence of this band at  $800\text{ cm}^{-1}$  is also consistent with the polymerization of HMDSO since  $\text{Si}-(\text{CH}_3)_2$  constitutes linear chains, in particular of the type  $(\text{CH}_3)-(\text{SiO}(\text{CH}_3)_2)_n-\text{Si}-(\text{CH}_3)_3$  within the polymer architecture.[4] Finally, it can also be noted that a very weak band appears on the polymer spectrum at  $2120\text{ cm}^{-1}$ . This new band can be assigned to stretching vibrations of  $\text{Si}-\text{H}$ , that can be produced by the monomer fragmentation.



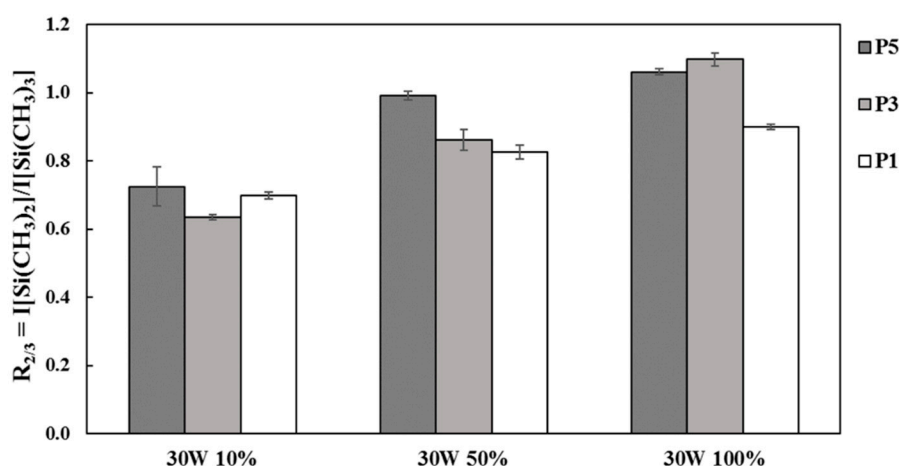
**Figure S4.** Typical ATR-FTIR spectrum of HMDSO (a) and HMDSO plasma polymer (deposited at DC =50% at P5) (b)

Besides, the comparison of the  $R_{O/I}$  ratios of the intensities of the bands at  $1260\text{ cm}^{-1}$  and  $1040\text{ cm}^{-1}$ , corresponding to  $\text{Si}(\text{CH}_3)_x$  and  $\text{SiOSi}$  groups respectively, before and after polymerization, is also consistent with a successful polymerization of HMDSO. Indeed, the value of  $R_{O/I} = I[\text{Si}(\text{CH}_3)_x]/I[\text{SiOSi}]$  decreases from about 0.9 for the monomer to about 0.6 for the plasma polymer. This result may originate from methyl abstraction during polymerization. When plasma polymers synthesized at various duty cycles and positions in the reactor were analyzed, no significant difference was observed for the value of the ratio  $R_{O/I} = I[\text{Si}(\text{CH}_3)_x]/I[\text{SiOSi}]$  (see Table S1).

**Table S1.** Values of  $R_{2/3}$  ratios corresponding to the intensities ratios of the bands at  $1260\text{ cm}^{-1}$  and  $1040\text{ cm}^{-1}$  (coming from  $\text{Si}(\text{CH}_3)_x$  and  $\text{SiOSi}$  groups respectively) measured in ATR FTIR spectra of HMDSO plasma polymers synthesized at different duty cycles and different positions in the reactor.

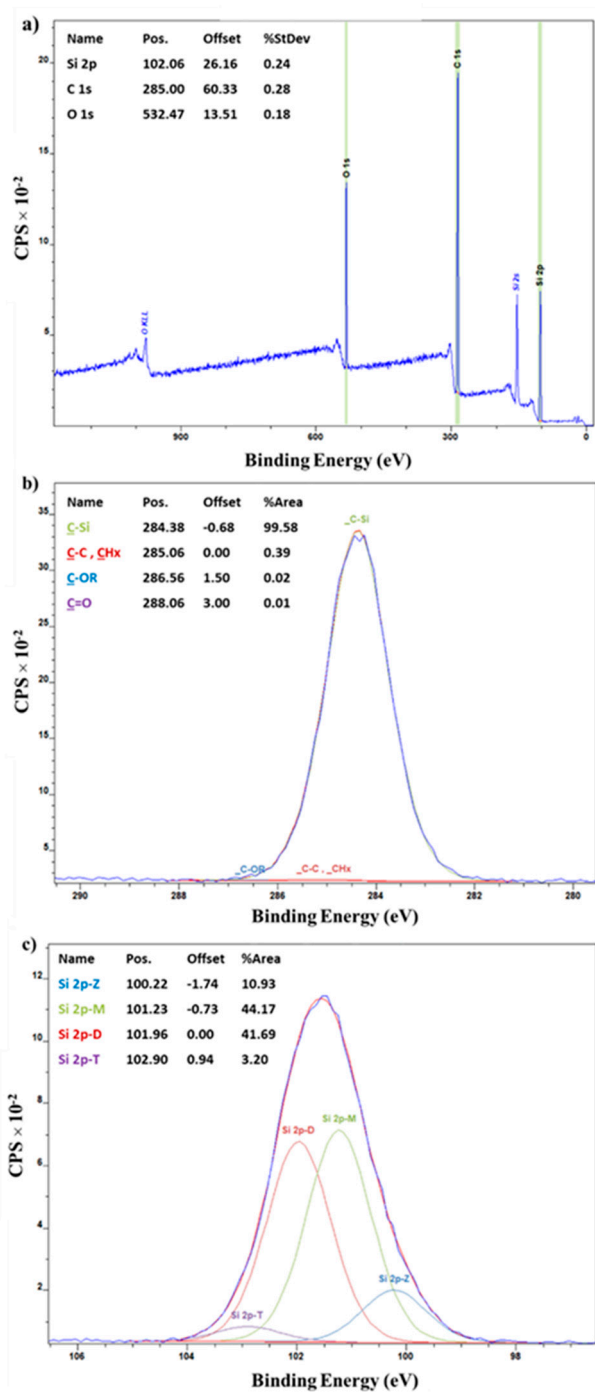
	30W 10%	30W 50%	30W 100%
P1	$0.58 \pm 0.01$	$0.63 \pm 0.02$	$0.64 \pm 0.01$
P3	$0.63 \pm 0.01$	$0.58 \pm 0.03$	$0.55 \pm 0.02$
P5	$0.64 \pm 0.06$	$0.61 \pm 0.01$	$0.58 \pm 0.01$

Besides, the  $R_{2/3}$  ratio of the intensities of the bands at  $800\text{ cm}^{-1}$  and  $840\text{ cm}^{-1}$ , corresponding to  $\text{Si}(\text{CH}_3)_2$  and  $\text{Si}(\text{CH}_3)_3$  groups respectively, can also provide useful information about monomer fragmentation during the deposition process and about the plasma polymer architecture.  $\text{Si}(\text{CH}_3)_3$  groups correspond to chain or branch ends in the polymer network whereas  $\text{Si}-(\text{CH}_3)_2$  is characteristic of linear chains, as already mentioned.[4] Therefore, a low value of  $R_{2/3} = I[\text{Si}(\text{CH}_3)_2]/I[\text{Si}(\text{CH}_3)_3]$  reflects low molecular weight chains and/or branched polymer architecture. It can be pointed out here that the overlapping of the characteristic band for the Si-O-Si bending vibrations, close to  $800\text{ cm}^{-1}$ , can be neglected since the intensity of the band related to the  $\text{CH}_3$  rocking vibrations in  $\text{Si}-(\text{CH}_3)_2$  is predominant as reported in the literature.[3] Figure S5 shows the calculated  $R_{2/3}$  ratios for plasma polymers obtained in the different operating conditions. They indicate a significant increase of this ratio by increasing the duty cycle which is consistent with higher fragmentation of HMDSO at higher energy, thus leading to less terminal  $\text{Si}(\text{CH}_3)_3$  groups.



**Figure S5.** Evolution of the  $R_{2/3}$  ratio of the intensities of the bands at  $800\text{ cm}^{-1}$  and  $840\text{ cm}^{-1}$  (coming from  $\text{Si}(\text{CH}_3)_2$  and  $\text{Si}(\text{CH}_3)_3$  groups respectively) measured in ATR FTIR spectra of HMDSO plasma polymers synthesized using different duty cycles at the different positions in the reactor.

Keeping in mind that the thickness of the probe layer is completely different for ATR-FTIR and XPS spectroscopies, complementary quantification of the surface chemical composition of HMDSO plasma polymers synthesized in different operating conditions was assessed using XPS. It should be noted that all polymer coatings that have been analyzed had a thickness higher than 100 nm, which enables to consider that the plasma polymer covers the entire surface of the substrate and that no signal comes from the latter on the spectra. Typical XPS spectra corresponding to the survey wide scan and high resolution of the C1s and Si2p peaks are presented in Figure S6.



**Figure S6.** Typical XPS survey wide scan (a) and high-resolution spectra of the C1s (b) and Si2p (c) peaks (showing also components fittings) of an HMDSO plasma polymer (deposited at DC = 50% at P3).

As expected, only Si, C, and O elements have been detected in all samples. Table S2 gives the atomic percentages of these elements, based on survey spectra, as well as the calculated C/Si and O/Si ratios of HMDSO plasma polymers deposited in different operating conditions. According to the XPS analyses, a C/Si ratio higher than 2 is calculated for all samples, indicating a relatively good conservation of the organic structure of the precursor, the initial

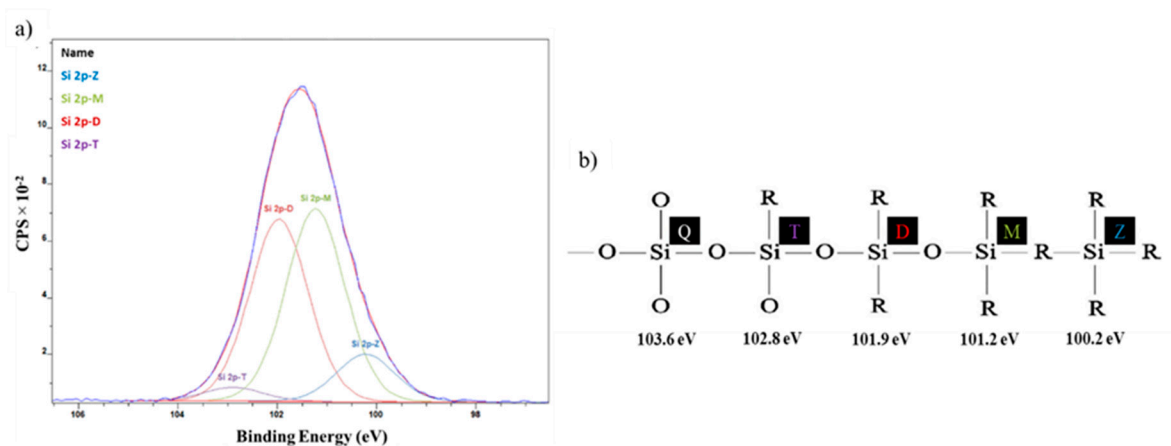
C/Si ratio in the precursor being equal to 3. Besides, an O/Si ratio close to the initial value of 0.5 is calculated for all plasma polymers synthesized by pulsed plasma polymerization. These results mean that methyl abstraction is relatively limited in pulsed plasma polymerization and that the plasma polymer network probably contains a good balance between Si–O–Si bridges and methylene bridges. However, it can be noted that a slightly higher O/Si ratio (from 0.52 to 0.62) was systematically calculated when plasma polymerization was conducted in continuous mode (DC = 100%). This increase in the oxygen content may come from a higher number of Si–O–Si bridges at the surface of the coating and/or a slight oxidation at the extreme surface at the end of the deposition process. Indeed, residual free radicals on the surface at the end of the polymerization, which are probably more numerous at high energy, may instantly react with atmospheric oxygen when the samples are recovered.

**Table S2.** Atomic percentages of Si, C, and O based on the survey spectra as well as the calculated C/Si and O/Si ratios of HMDSO plasma polymers deposited in different operating conditions.

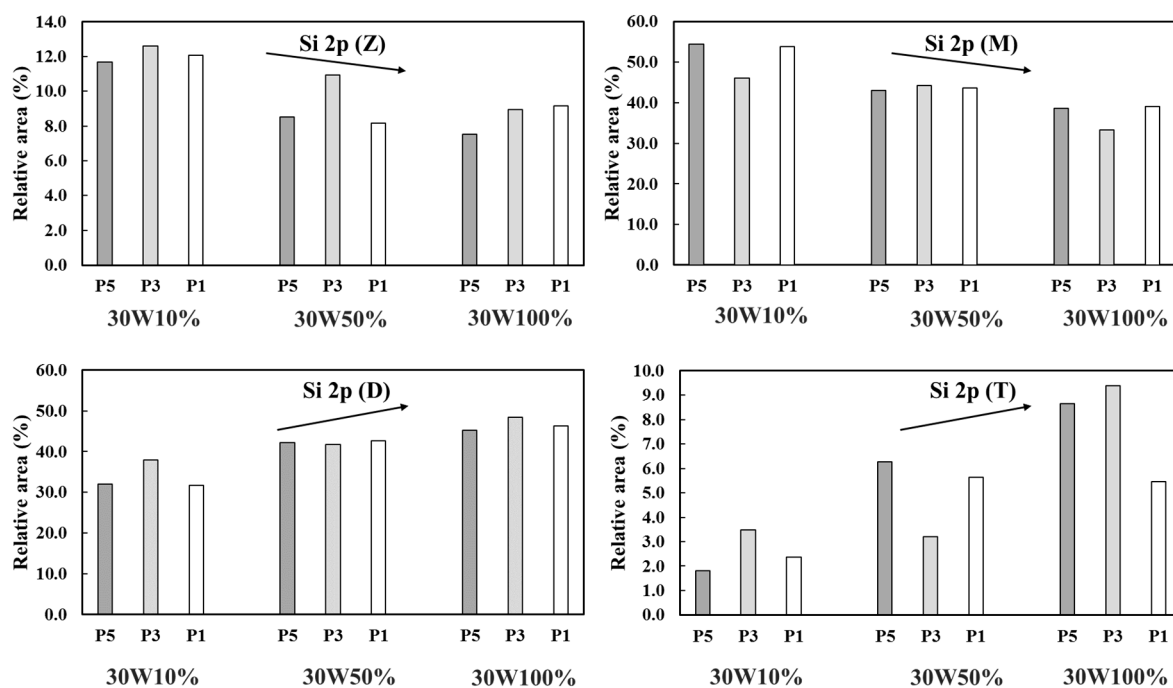
DC [%]	Position	C [at %]	O [at %]	Si [at %]	C/Si	O/Si
10	P1	61.25	12.77	25.98	2.36	0.49
10	P3	59.30	13.53	27.17	2.18	0.50
10	P5	61.70	12.37	25.92	2.38	0.48
50	P1	62.46	12.47	25.08	2.49	0.50
50	P3	60.33	13.51	26.16	2.31	0.52
50	P5	61.86	12.8	25.34	2.44	0.51
100	P1	61.25	13.26	25.49	2.40	0.52
100	P3	57.86	16.15	25.99	2.23	0.62
100	P5	63.38	13.94	22.68	2.79	0.61

To obtain further quantitative data about the chemical composition of the plasma polymer network, high-resolution spectra of Si2p peak were deconvoluted to determine the chemical environment of silicon atoms in the siloxane structures, as shown in Figure S7.a. The deconvolution method is based on the work of Alexander *et al.*[6] Four different chemical states of silicon atoms have been considered according to the number of oxygen atoms bound to the silicon: M, D, T and Q which are linked with one, two, three and four oxygen atoms, respectively (Figure S7.b). However, this methodology was not sufficient to fit perfectly all experimental data. As shown in Figure S7, an additional contribution centered at 100.2 eV was required, which is assumed to come from silicon atoms bound to none oxygen atoms (labeled Z), as already reported by Roualdes *et al.*[7,8] The Si2p peak deconvolution was thus performed by considering five components, labeled Z, M, D, T and Q, centered at 100.2 eV, 101.2 eV, 101.9 eV, 102.8 eV and 103.6 eV respectively.





**Figure S7.** a) Deconvolution of high-resolution spectra of the Si2p of HMDSO plasma polymer and b) silicon chemical environments and respective binding energies considered for this deconvolution.



**Figure S8.** Relative areas of different silicon chemical states identified in the high-resolution Si2p peak (measured by XPS) of HMDSO plasma polymers prepared using different duty cycles at different positions in the reactor.

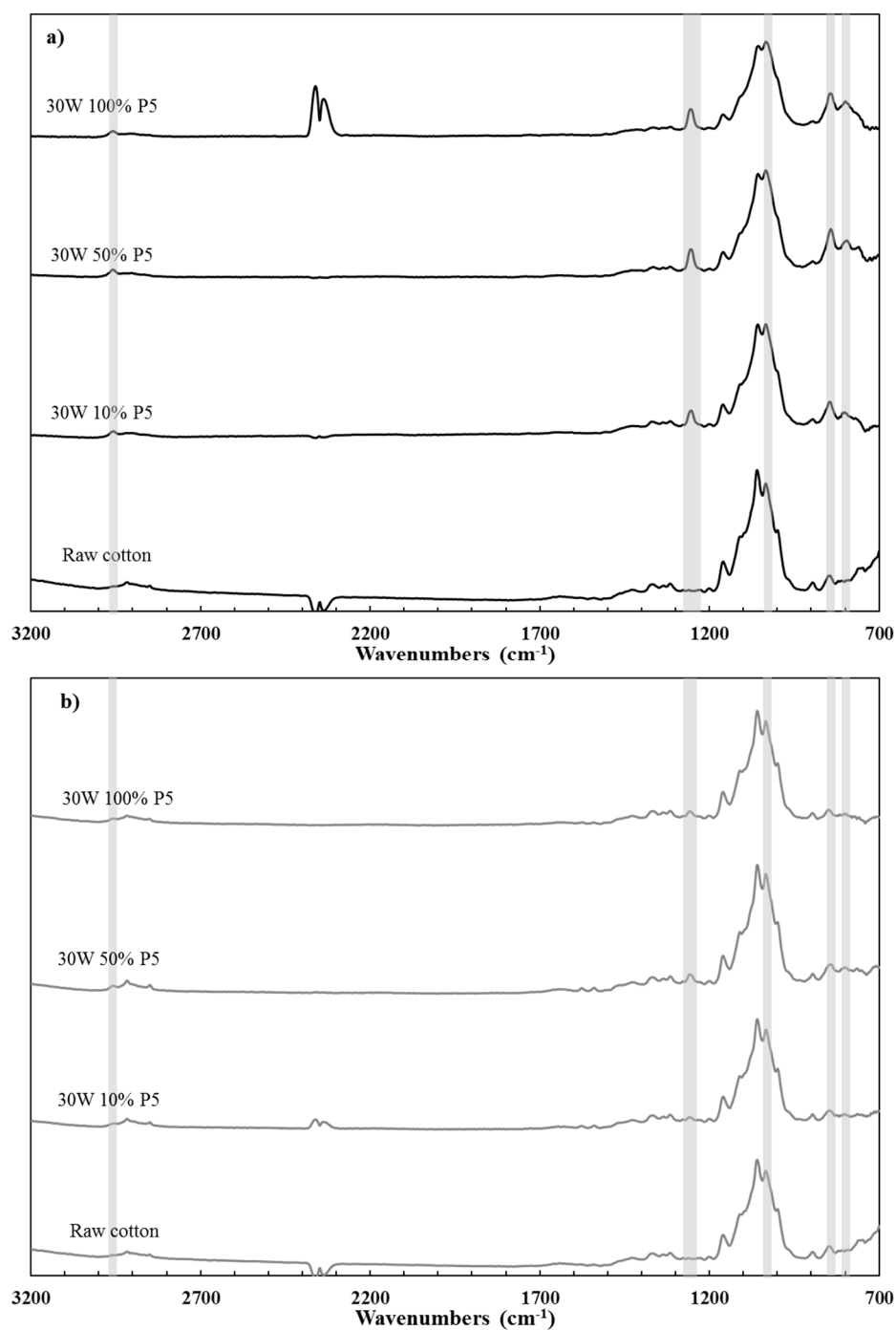
Figure S8 summarizes the calculations of the relative areas of each Si2p component by using fitting results obtained for the different coatings. First, it can be noted that the Q component was not observed whatever the operating condition of plasma polymerization. This is in accordance with the high amount of carbon detected as well as the low O/Si ratios calculated for all samples. The main siloxane units that have been detected correspond to the M and D

components. These findings indicate a limited fragmentation of the monomer and the formation of rather organic polymers with relatively low molecular weight chains or at least branched architectures with many terminal units as well as low crosslinking *via* Si–O–Si bridges. A tendency could be observed when increasing the duty cycle: the contributions of the Z and M components slightly decrease whereas the contributions of the D and T ones slightly increase. These results are in agreement with the interpretations made from XPS wide scan spectra. However, no clear tendencies can be observed regarding the different positions in the reactor. Therefore, it can be concluded that higher energies, reached by increasing the duty cycle of the generator up to a continuous mode, imply as expected a slightly more crosslinked plasma polymer network through methyl abstraction. On the contrary, a low duty cycle favors the presence of terminal units (Si-(CH<sub>3</sub>)<sub>3</sub>) within the macromolecular architecture. It should however be noted that the oxygen content is very low in plasma polymers obtained in the whole experimental condition range, which could imply the presence of a significant amount of methylene bridges to form the polymer network.

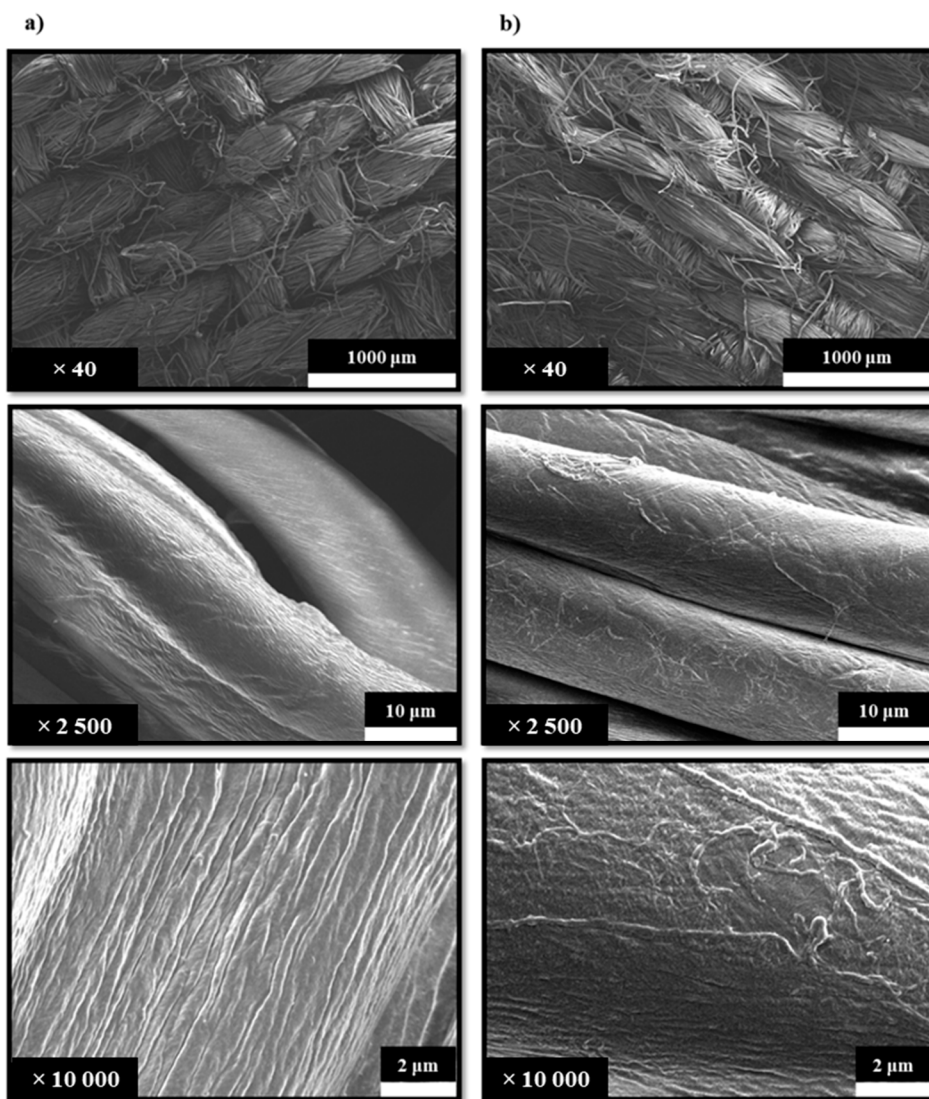
The thorough investigations of the chemical structure of the HMDSO plasma polymers synthesized under different conditions revealed that the duty cycle has a noticeable impact on the properties of the final coating, highlighting the temporal dependence of plasma polymerization. The spatial dependence seems to be less pronounced from a chemical point of view but is still considered when plasma polymerization of HMDSO was performed on cotton fabrics.

#### **Presence of plasma polymer coatings (synthesized with HMDSO) on cotton fabrics after washing**

Figure S9 presents the evolution of ATR-FTIR spectra of cotton fabrics treated by plasma polymerization of HMDSO performed at different duty cycles (10%, 50%, 100%) at position P5 before and after washing; results for cotton fabrics treated in other positions in the reactor showing similar tendencies. Even if no precise quantification of the chemical composition of HMDSO plasma polymers is possible, due to the strong overlapping of characteristic bands of cotton with relevant bands from the plasma polymer, it is possible to see that the chemical fingerprint of HMDSO plasma polymer does not seem to be altered after washing, when bands from the polymer are still visible. ATR-FTIR spectra enable verification of at least the presence or not of the polymer on textile fabrics after washing. A noticeable decrease in the absorbance of characteristic bands of HMDSO plasma polymers and in particular the band at 1260 cm<sup>-1</sup> is observed after 10 washing cycles. The disappearance of this band can even be noted for the lowest duty cycle (10%), which is in agreement with the wettability tests previously reported. This result is in accordance with a “quasi-complete” removal of the HMDSO plasma polymer coating from the cotton surface in this condition. For the samples prepared at other duty cycles, the chemical fingerprint of the plasma polymer can still be observed with relatively high absorbance, in particular for the samples prepared with a DC = 50%, which correlates quite well with the results of water contact angle measurements.

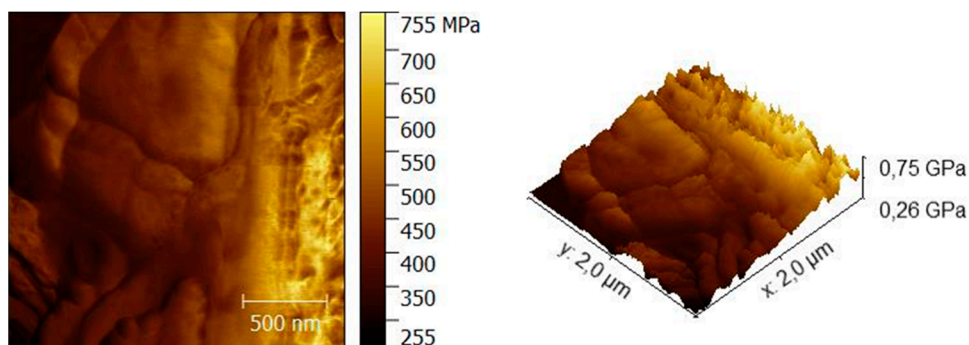


**Figure S9.** ATR-FTIR spectra of untreated cotton fabrics and treated ones with HMDSO plasma polymers deposited at different duty cycles (solely spectra obtained at position P5 are shown but similar tendencies have been observed for other positions) before (a) and after 10 washing cycles (b). Wavelength ranges corresponding to positions of characteristic bands of HMDSO plasma polymers have been highlighted in gray to facilitate the reading.



**Figure S10.** SEM images at different magnifications of untreated cotton textile fabrics before (a) and after 10 washing cycles (b).

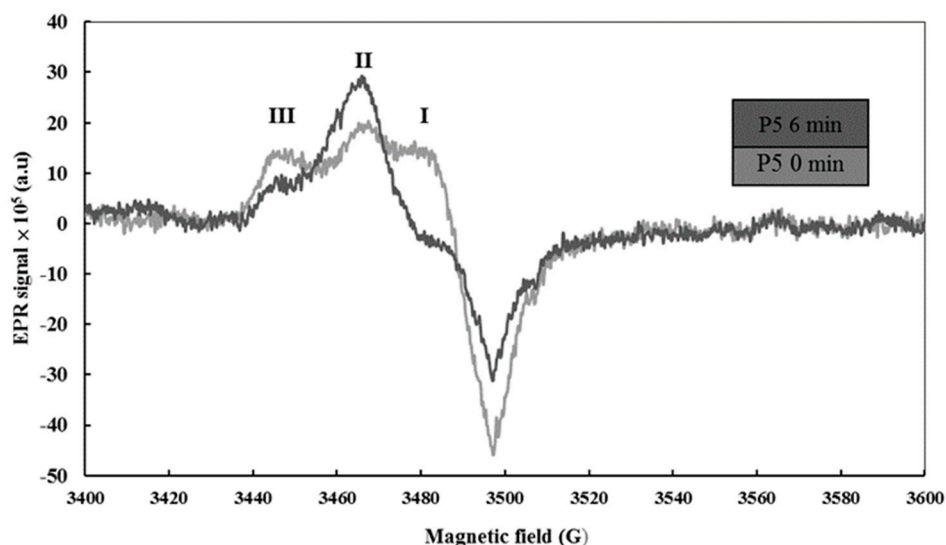
### Estimation of the Young's modulus of the cotton fiber by AFM in Peak Force QNM mode



**Figure S11.** 2D and 3D elastic modulus mapping of a single cotton fiber obtained by AFM in Peak Force QNM mode.

## **Evaluation of the stability of the radicals observed by EPR spectroscopy**

To prove that the difference in terms of EPR signal intensities, in particular for the third species, did not originate from differences in the handling of samples starting from the opening of the reactor and the end of the EPR spectroscopy analysis, the EPR spectrum of the sample prepared at P5 was recorded a second time after 6 minutes. Figure S12 presents the two spectra recorded for this sample and shows that the intensities of the signals corresponding to species II and III remain visible despite this delay in the spectrum measurement, which indicates that these species correspond to relatively long-life radicals on cotton fabrics. It is thus reasonable to discuss the difference in signal intensities corresponding to these third species observed between the different samples.



**Figure S12.** EPR spectra of cotton fabrics treated at DC = 50% and P5 measured directly after sample retrieval from the reactor and 6 minutes after.

## **References**

- [1] J. Zimmermann, F.A. Reifler, G. Fortunato, L.-C. Gerhardt, S. Seeger, A Simple, One-Step Approach to Durable and Robust Superhydrophobic Textiles, *Adv. Funct. Mater.* 18 (2008) 3662–3669. <https://doi.org/10.1002/adfm.200800755>.
- [2] C. Chung, M. Lee, E. Choe, Characterization of cotton fabric scouring by FT-IR ATR spectroscopy, *Carbohydr. Polym.* 58 (2004) 417–420. <https://doi.org/10.1016/j.carbpol.2004.08.005>.
- [3] P. Raynaud, B. Despax, Y. Segui, H. Caquineau, FTIR Plasma Phase Analysis of Hexamethyldisiloxane Discharge in Microwave Multipolar Plasma at Different Electrical Powers, *Plasma Process. Polym.* 2 (2005) 45–52. <https://doi.org/10.1002/ppap.200400034>.
- [4] R.A. Siliprandi, S. Zanini, E. Grimoldi, F.S. Fumagalli, R. Barni, C. Riccardi, Atmospheric Pressure Plasma Discharge for Polysiloxane Thin Films Deposition and Comparison with Low Pressure Process, *Plasma Chem. Plasma Process.* 31 (2011) 353–372. <https://doi.org/10.1007/s11090-011-9286-3>.

- [5] G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, John Wiley & Sons, 2004.
- [6] M.R. Alexander, R.D. Short, F.R. Jones, W. Michaeli, C.J. Blomfield, A study of HMDSO/O<sub>2</sub> plasma deposits using a high-sensitivity and -energy resolution XPS instrument: curve fitting of the Si 2p core level, *Appl. Surf. Sci.* 137 (1999) 179–183. [https://doi.org/10.1016/S0169-4332\(98\)00479-6](https://doi.org/10.1016/S0169-4332(98)00479-6).
- [7] S. Roualdes, R. Berjoan, J. Durand, <sup>29</sup>Si NMR and Si2p XPS correlation in polysiloxane membranes prepared by plasma enhanced chemical vapor deposition, *Sep. Purif. Technol.* 25 (2001) 391–397. [https://doi.org/10.1016/S1383-5866\(01\)00067-3](https://doi.org/10.1016/S1383-5866(01)00067-3).
- [8] G. Dakroub, T. Duguet, J. Esvan, C. Lacaze-Dufaure, S. Roualdes, V. Rouessac, Comparative study of bulk and surface compositions of plasma polymerized organosilicon thin films, *Surf. Interfaces.* 25 (2021) 101256. <https://doi.org/10.1016/j.surfin.2021.101256>.