

## HYDROPHOBIC FUNCTIONALIZATION OF CELLULOSIC SUBSTRATES USING ATMOSPHERIC PRESSURE PLASMA

KARTICK K. SAMANTA, T. N. GAYATRI, S. SAXENA, S. BASAK, S. K. CHATTOPADHYAY, A. ARPUTHARAJ and V. PRASAD

*Plasma Nanotechnology Laboratory, Chemical and Bio-chemical Processing Division,  
Central Institute for Research on Cotton Technology, Adenwala Road, Matunga,  
Mumbai, 400019, India*

✉ *Corresponding author: Kartick K. Samanta, karticksamanta@gmail.com*

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In the present study, without using water as a processing medium, a hydrophilic cotton (cellulosic) textile was plasma treated in an indigenously developed atmospheric pressure plasma reactor in the presence of helium-fluorocarbon (He-FC) gases, for imparting hydrophobic functionality to the treated textile. The optical emission spectra (OES) showed the fragmentation of fluorocarbon molecule with atomic lines of F at 429 nm, 357 nm, 341 nm, 325 nm and  $-CF_2$  line at 318 nm. After the plasma treatment, the hydrophilic cotton turned into a highly hydrophobic one, and as a result, a water droplet of 37  $\mu$ l was not absorbed by the fabric even after 60 min, in contrast to the untreated fabric, which absorbed the water droplet within 0.05 min. The applied finish was found to be durable to soap washing. The ATR-FTIR analysis showed the presence of various  $-CF_x$  molecules in the plasma treated sample and about 4.2% fluorine atom was detected on the surface of the plasma treated sample by EDX analysis. The secondary ion mass spectrometry (SIMS) analysis showed the presence of a strong molecular peak of  $F^-$  at 19 amu, in addition to significant decreases in  $O^-$  and  $OH^-$  molecular peaks at 16 and 17 amu, respectively, in the plasma treated sample. Both scanning electron microscope (SEM) images (physical) and SIMS chemical images (molecular) have ruled out any blockage of inter-fibre spacing inside the fabric structure, confirming this as a nano-scale surface modification of textiles. It is inferred that the hydrophilic cotton cellulose has turned into a hydrophobic one after the plasma treatment, primarily due to the incorporation of various fluorocarbon and hydrocarbon molecules in the cellulose, besides the removal of a large number of hydroxyl groups from it.

**Keywords:** cellulosic textile, fluorocarbon, hydrophobic, nano-scale surface modification, plasma

### INTRODUCTION

Wet chemical processing of textile is important, as it improves the aesthetic and functional value of textiles. However, the process is water and energy intensive. To process one kilogram of cotton textiles, roughly a hundred litres of water are used, which is finally discharged as an effluent contaminated with unused dyes, pigments, and other hazardous to non-hazardous chemicals. Any such discharge has a serious impact on the flora and fauna, besides its adverse effect on the fertility of agricultural land. The shortage of water in the near future will have a serious impact on the textile chemical processing sector. Therefore, textile industries are now slowly but progressively moving towards the implementation of water-less or low-water based processing technologies, such as digital printing,

spray and foam finishing, and plasma processing. The main attraction of plasma in an industrial application is that it allows avoiding liquid effluents. Some other advantages include saving large quantities of water, chemicals and energy. Plasma, an ionized gas, can be used for nano-scale surface engineering of textiles in a dry state within a few seconds to a minute. The surface modification of textiles is carried out by its activation using helium, argon, oxygen, nitrogen and air plasma. The generation of radicals on the fibre surface, followed by plasma reaction of a precursor molecule with hydroxyl, carbonyl, carboxyl, fluorocarbon, and acrylate backbone can provide a pathway for development of value-added textiles exhibiting properties like water, stain and oil repellency, hydrophilicity, *Cellulose Chem. Technol.*, **50** (7-8), 745-754 (2016)

antimicrobial, flame retardant, and ultraviolet (UV) ray protection.<sup>1-3</sup> A plasma treatment can also be used to improve dyeing, printing and adhesion strength of the textile and so far, mainly low-pressure plasmas have been used for such applications. However, the low-pressure plasma technology has not found much favour commercially in the textile fields, as it is inherently limited to batch processing, and requires small sample size, long treatment time, and complicated maintenance of the expensive vacuum system. On the contrary, atmospheric pressure plasma is an emerging technology that can overcome the limitations of low-pressure plasma technology and has been explored for antibacterial activity, improvement of liquid absorbency, improvement in adhesion, desizing, dyeing and printing, and sterilization.<sup>4-10</sup> Hydrophobic modification of cellulosic textiles is desirable for their protection from liquid contaminants in various applications. It has been achieved using various hydrocarbon and silicone precursors in vacuum or atmospheric pressure plasma.<sup>11-12</sup> However, fluorocarbon chemicals are found to be more effective compared to hydrocarbon or silicones for hydrophobic finishing of textile substrates. A few studies on hydrophobic functionalization of cellulosic textile using different fluorocarbon gases using atmospheric pressure plasmas have recently been reported.<sup>13</sup> However, very limited information is available on the effects of different process parameters on plasma reaction, as well as the role of fluorocarbon based plasma chemistry on cellulosic substrates.

In this study, hydrophobic finishing of a cellulosic textile has been carried out by an *in-situ* plasma reaction, using commercially available fluorocarbon R410 gas, which is a mixture of penta-fluoro ethane and di-fluoro methane, at the atmospheric pressure. The plasma species have been analysed in real-time using an optical emission spectrometer, and the surface chemistry of the plasma treated textile has been studied in details using a secondary ion mass spectrometer (SIMS).

## EXPERIMENTAL

### Materials

A desized and bleached cotton woven textile, with an areal density of 0.123 g/cm<sup>2</sup>, having 43 ends per cm in the warp direction and 36 picks per cm in the weft direction, was used as substrate. Prior to the plasma treatment, the fabric was rinsed in acetone and dried in

an air-oven at 90 °C for 10 min, so as to remove any contaminants and trapped moisture from the textile structure. Helium (He) was procured from Alchemie gases Pvt. Ltd. (Mumbai, India) and commercial fluorocarbon R410 gas (mixture of 50% pentafluoro ethane and 50% difluoro methane) was purchased from Industrial Compressor Component Company, also located in Mumbai.

### Plasma treatment

The plasma treatment was carried out using an indigenously developed atmospheric pressure plasma reactor in the presence of helium-fluorocarbon (He-FC) gases. Plasma was generated in between two rectangular aluminum electrodes (7 cm × 6 cm) at a discharge voltage and frequency of 4-6 kV and 21.8 kHz, respectively. During the plasma treatment, the helium gas flow rate was kept at 600 ml/min and fluorocarbon at 200 ml/min by using two mass flow controllers made by Alicat Scientific, USA.

### Measurement of water absorbency time and contact angle

The water absorbency time of the fabric was measured according to the AATCC 79-2007 method. A water droplet of 37 µl was placed on the fabric that was being held in the horizontal position supported in a frame. The time for the water droplet to get fully absorbed by the fabric was recorded. The water contact angle was measured by the sessile drop method. A photograph of the water droplet was taken using a Cannon EOS 60 D SLR camera. A light source was kept behind the water droplet to enhance its boundary for precise measurement of the contact angle. The volume of the water droplet for contact angle measurement was kept at 3.4 microlitres (µl).

### Optical emission spectroscopy (OES) of plasma

Light emitted by the excited atoms and molecules over the wavelength of 300 to 800 nm was analyzed using an Optical Emission Spectrometer (OES), Mikropack model PlasCalc 2000. The offline analysis of OES data was carried out using Specline 2.1 software.

### Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) analysis

The ATR-FTIR analysis of both the untreated and helium-fluorocarbon (He-FC) plasma treated samples was carried out on an FTIR-Prestige 21 Shimadzu spectrometer fitted with HATR multiple reflection accessories, using a ZnSe prism.

### Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) analyses

The surface micrographs of the different samples were studied using a Field Emission Gun Scanning Electron Microscope (FEG-SEM), Model: JSM-7600F at a magnification of 5000 KX. The samples were gold

coated prior to analysis. The EDX analysis of the samples was also carried out using the same equipment.

#### Secondary ion mass spectrometry (SIMS)

The surface chemical composition of the untreated and the plasma treated samples at about 2 nm level from the top surface was analyzed using a secondary Ion Mass Spectrometer (SIMS), Model PHI TRIFT V nanoTOF, using gold as a primary ion source.

#### Durability and ageing study

The 12-min helium-fluorocarbon (He-FC) plasma treated sample was studied for durability of the imparted finish to soap washing. The sample was washed as per the AATCC-61-2008 2A method, at 49 °C in the presence of 50 steel balls, where one washing cycle was considered to be equivalent to five home laundry washes. Thereafter, the sample was thoroughly washed in distilled water, dried and tested for water absorbency. Similarly, aging tests were conducted by keeping the sample at the ambient or fixed (70 °C) temperature, and varying time duration. Then, the water absorbency time was measured in each case.

## RESULTS AND DISCUSSION

### Generation of plasma and its optical properties

Atmospheric pressure plasmas were generated in the presence of both helium (He) and helium-fluorocarbon (He-FC) gases. It was observed that it was easy to generate plasma in the presence of pure helium (He) at a voltage of 4 kV with a gas flow of 200 ml/min. However, an admixture of fluorocarbon gas with He disturbs the plasma zone. Therefore, to generate He-FC plasma, the discharge voltage was increased to 6 kV and the gas flow rate to 800 ml/min (He at 600 ml/min and FC at 200 ml/min).

The colour of a particular plasma depends on the atomic and molecular species present in the plasma zone and on the photons emitted by the excited species. As every gas has a distinct emission characteristic in the excited state, each one produces a particular colour. For example, when He was ionized, it gave a light bluish purple colour, as shown in Figure 1 (a). Visually, it looks like a uniform plasma, free from any micro-discharge. However, when fluorocarbon gas was

introduced along with He, its colour changed to bluish (Fig. 1 (b)). It was also a uniform plasma and free from any micro-discharge.

Plasma is an ionized gas composed of ions, electrons, neutrals, excited particles, UV-light and photon. Therefore, the light emitted by the excited atoms and molecules over the wavelength of 200 to 800 nm was analyzed using the Optical Emission Spectrometer (OES) in real-time to understand the related plasma chemistry. The OES spectrum of helium (He) showed the presence of atomic lines at the wavelengths of 705 nm, 666 nm, 654 nm, 585 nm, 726 nm, 388 nm, 356 nm and 501 nm, as shown in Figure 2. Among the various atomic lines of He, the 705 nm line is the strongest one. However, when fluorocarbon (FC) gas was introduced along with He, there were several changes in the OES spectrum. In the presence of fluorocarbon, He showed a strong atomic peak at 666 nm, instead of 705 nm, as shown in Figure 3. It can also be seen that the He line at 654 nm present in He plasma (Fig. 2) did not appear in He-FC plasma (Fig. 3) and the intensity of several fluorine peaks was higher than the intensity of various peaks of He. Some of the atomic lines of fluorine and fluorocarbon species are F at 429 nm, F at 357 nm, F at 341 nm, F at 325 nm, CF<sub>2</sub> at 318 nm and F at 311 nm. This indicated fragmentation of fluorocarbon in the plasma zone into smaller species.

Table 1 shows the ratio of atomic lines of He in pure helium (He) to the mixture of helium-fluorocarbon (He-FC) plasma. It can be seen that the ratio of He 705/666 nm lines decreased from 8.5 in He plasma to 0.5 in He-FC plasma. A similar result was also observed for He 705/585 nm lines, where it decreased from 9.8 to 0.7. However, there was a little increase in the ratio of He 666/585 nm lines from 1.1 to 1.4. Such change in the intensity of helium lines in He and He-FC plasma indicates different patterns of He ionization based on whether it is pure He or a mixture with fluorocarbon gases.

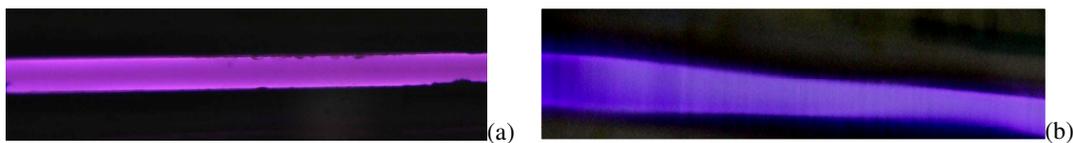


Figure 1: Colour of (a) helium and (b) helium-fluorocarbon (He-FC) plasma

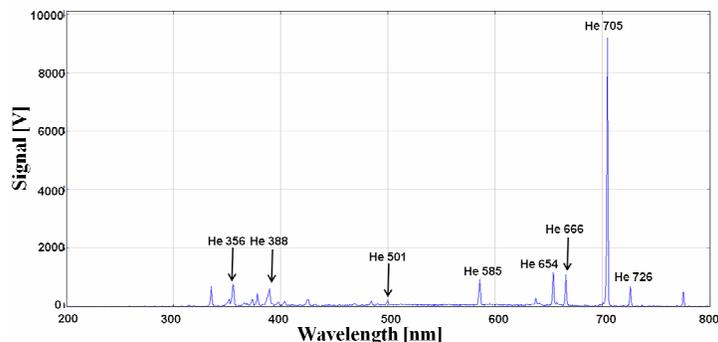


Figure 2: Optical emission spectrum (OES) of helium (He) plasma

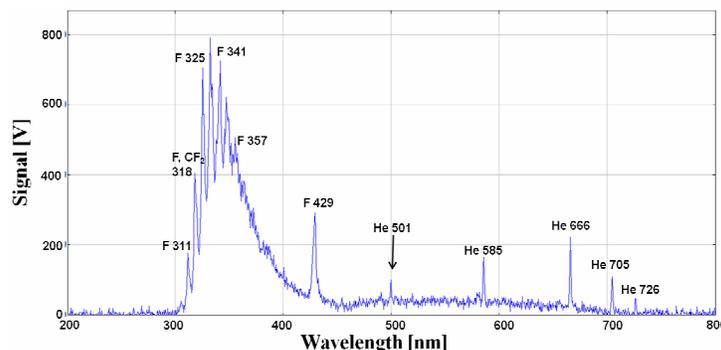


Figure 3: Optical emission spectrum (OES) of helium-fluorocarbon (He-FC) plasma

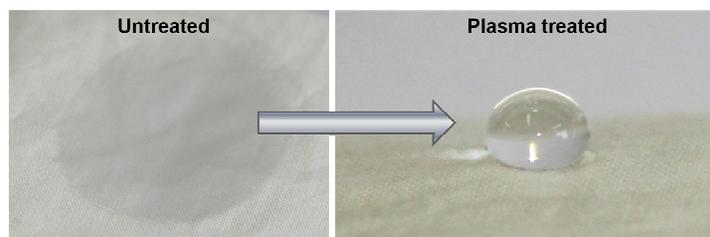


Figure 4: Conversion of hydrophilic cotton to hydrophobic cotton by plasma treatment

Table 1  
Ratio of intensity of helium atomic lines in He and He-FC plasma

Plasma	He 705/666 nm	He 705/585 nm	He 666/585 nm
Helium (He)	8.5	9.8	1.1
Helium-fluorocarbon (He-FC)	0.5	0.7	1.4

### Hydrophobic finishing of textiles

Cold plasma at atmospheric pressure was generated in the presence of helium-fluorocarbon gases and was utilized to improve the hydrophobic functionality of cellulosic cotton textiles. It was observed that after the plasma reaction, the hydrophilic cotton turned into a hydrophobic one (Fig. 4). The effect of the plasma treatment time on the water absorbency of the cotton textile is presented in Table 2. It can be seen that after 1 min of plasma treatment, the

water absorbency time increased to 2.5 min in the treated sample from 0.05 min (*i.e.* 3 s) observed in the untreated sample. With further increase in the plasma treatment time, the water absorbency time was found to increase exponentially.

After 9 min of the plasma treatment, the water absorbency time increased to 17 min and after 12 min, the sample showed a water absorbency time of more than 60 min. The measurement was continued up to 60 min, as with a water absorbency time of 60 min or more for a textile is

normally considered an excellent hydrophobic property. Such an exponential rise in the water absorbency time of the textile, upon increasing the plasma treatment time, signifies the involvement of a greater amount of fluorocarbon gas, which is responsible for the better hydrophobic functionality of the textile. It can also be seen that a minimum of 2400 ml of fluorocarbon (FC) gas was necessary to impart an excellent hydrophobic functionality in the cotton textile with an absorbency time >60 min. Similar to the water absorbency time, the water contact angle also significantly increased from  $\sim 0^\circ$  in the untreated sample to  $142^\circ$  in the 12-min plasma treated sample. After the plasma treatment, the hydrophilic cotton turned into a hydrophobic one, mainly due to the attachment of different fluorocarbon species, such as  $-F$ ,  $-CF$ ,  $-CF_2$  and  $-CF_3$ , and other hydrocarbon molecules with the cellulose polymer, as discussed below.

The 12-min plasma treated sample was subjected to standard soap washing cycles, as per the AATCC-61-2008 2A method. The water absorbency time in the plasma treated un-washed sample was >60 min. After 5 cycles of home laundering, it slightly reduced to 45 min and further, to 13.5 min after 10 washing cycles. It was further observed that after 20 and 30 cycles of laundering, the water absorbency times were 5.5 and 4 min, respectively. However, the residual hydrophobicity of 4 min after 30 washing cycles was still significantly higher compared to 3 s (0.05 min) measured in the untreated sample. It was also interesting to observe that a part of the lost hydrophobicity could be retrieved by a heat treatment of the sample. The water absorbency time in the 30 times washed sample upon heat treatment at  $90^\circ\text{C}$  for 15 min was found to increase from 4 min to 31 min. This phenomenon indicates that during the soap washing, not all of the hydrophobic functional groups are permanently lost; a significant number of them probably rearrange themselves in such a manner

as to remain inaccessible at the surface of the fibres, after repeated soap washings in the presence of a surfactant. However, these groups can be reverted during the heat treatment, and a similar observation has been reported in the literature.<sup>14</sup> The results indicate that the imparted hydrophobic functionality is quite durable to repeated laundry washing. It implies that fluorocarbon molecules must have chemically attached to the cellulosic textile by forming covalent bonds, rather than by a simple and superficial surface deposition.

Similarly, when the plasma treated sample was stored at an ambient temperature for more than three months, there was no change in hydrophobicity, *i.e.*, in the water absorbency time. Further, when the sample was subjected to a heat treatment at  $90^\circ\text{C}$  for up to 7 hours, there was also no noticeable change in water absorbency time. However, there was a decrease in the water absorbency time from >60 min to 26.5 min, when the sample was kept at  $90^\circ\text{C}$  for 15 hours. This was possibly caused by the partial damage of the cellulosic textile and of the imparted finish that occurred at that elevated temperature during much longer time of the treatment, as evidenced by the onset of yellowing of the sample.

#### Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) analysis

It was observed that with increasing the time duration of the plasma treatment of the textiles, there was a constant improvement in the water absorbency time. The ATR-FTIR curve shows the presence of different fluorocarbon species in the plasma treated samples, such as the absorption peak of  $>C=CF_2$  at  $1750\text{ cm}^{-1}$ ,  $-CF$  stretching in  $-CF_2CF_3$  at  $1368\text{ cm}^{-1}$ ,  $-CF_2$  asymmetric stretching at  $1270\text{ cm}^{-1}$ ,  $-CF_2$  symmetric stretching at  $1160\text{ cm}^{-1}$  and  $-CF_3$  absorption at  $970\text{ cm}^{-1}$  (Fig. 5). It is well known that  $-CF$ ,  $-CF_2$  and  $-CF_3$  containing moieties have lower surface energy and they can impart hydrophobic functionality.

Table 2  
Effect of plasma treatment time on water absorbency of cotton fabric

He flow rate (ml/min)	Fluorocarbon flow rate (ml/min)	Plasma treatment time (min)	Total fluorocarbon flow (ml/min)	Water absorbency time (min)
600	200	0	0	0.05
600	200	1	200	2.50
600	200	3	600	9.00
600	200	6	1200	11.00
600	200	9	1800	17.00
600	200	12	2400	> 60

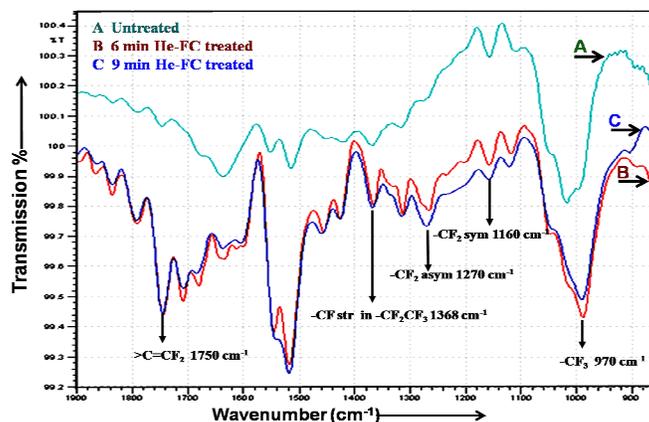


Figure 5: ATR-FTIR spectra of (A) untreated, (B) 6-min He-FC plasma treated, and (C) 9-min He-FC plasma treated samples

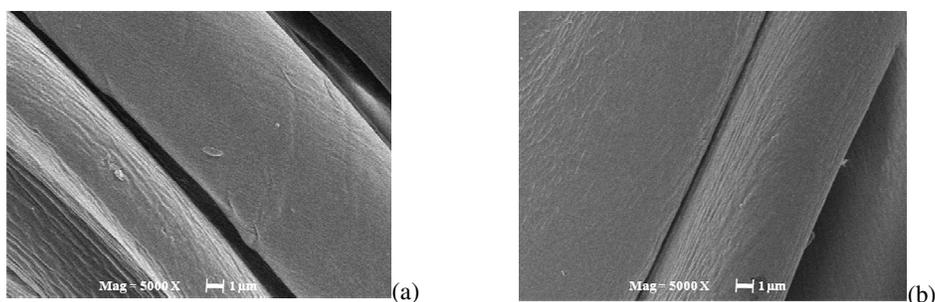


Figure 6: SEM micrograph of (a) untreated and (b) He-fluorocarbon treated samples

Table 3  
Surface atomic percentage in various cotton textiles

Element	Atomic percentage	
	Untreated	Plasma treated
C	55.5	52.1
O	44.5	43.7
F	0.0	4.2

These peaks appeared on the surface of the cotton fibres after the plasma reaction of helium-fluorocarbon (He-FC), resulting in an increase in the absorption intensity, *i.e.*, the decrease in transmission intensity. The curves B and C (Fig. 5) showed a similar result, as there was not much difference in the water absorbency time in the 6- and 9-min He-FC treated samples. The result indicates the fragmentation of pentafluoro ethane and difluoro methane in the plasma zone and their reaction with the cellulose polymer of the cotton textile.

#### Scanning electron micrograph (SEM) and energy-dispersive X-ray (EDX) spectroscopy analysis

From Figure 6 (a), it can be seen that the untreated sample has a smooth surface

morphology. The 12-min helium-fluorocarbon (He-FC) plasma treated sample also has similar surface morphology (Fig. 6 (b)), though its surface has become highly hydrophobic. In both the fabric samples, the individual fibres are easily visible along with their bean shape structure. This implies that plasma modification has happened on the fibre surface at a nanometer level, without blocking/covering the intra-fibre or inter-fibre spacing and other pores. This observation is important as it assures that the hydrophobicity imparted to the cotton textile by the plasma treatment will in no way compromise the comfort properties of the cotton textiles, in terms of air permeability and moisture vapour permeability.

Table 3 shows the presence surface atoms in percentage for both the untreated and the 12-min plasma treated samples, as determined by the

energy dispersive X-ray spectroscopy. Cotton is cellulosic in nature, and it consists of carbon, oxygen and hydrogen atoms. As EDX cannot detect the hydrogen (H) atom, only peaks for carbon and oxygen were noted. It can be seen that the untreated cotton has 44.5% oxygen and 55.5% carbon, which is similar to the theoretical value of oxygen and carbon contents reported in the literature for the cellulosic substrate.<sup>11</sup> On the contrary, in the plasma treated sample, about 4.2% fluorine was detected and the oxygen percentage was found somewhat lower, of 43.7%. The appearance of fluorine peaks and the decrease in oxygen percentage are indicative of the reaction of various fluorocarbon species with cotton cellulose, as discussed already during the ATR-FTIR analysis. The reduction of the surface oxygen percentage in the plasma treated sample was possibly due to the depletion of  $-OH$  molecules of the cellulose, aiding it to become hydrophobic in character.

### Secondary ion mass spectrometry (SIMS) analysis

Mass spectra were used to analyze the surface molecules and their relative abundance in both the untreated and (He-FC) plasma treated samples. Figure 7 shows the negative ion mass spectrum of the untreated sample with the major peaks at 1 amu for  $H^-$ , 12 amu for  $C^-$ , 13 amu for  $CH^-$ , 16 amu for  $O^-$ , and 17 amu for  $OH^-$ . In addition to these, other mass peaks are: 25 ( $CH-C^-$ ), 41, 45, 59, 71, and 87 amu. These imply that during the SIMS analysis, the groups in the cellulose, such as  $-CH_2OH$ ,  $-CHOH$ ,  $-CHOH-CHOH-$  etc., were broken down into the smaller fragments, such as  $H^-$ ,  $C^-$ ,  $CH^-$ ,  $O^-$ ,  $HO^-$ ,  $C-CH^-$ , and so on.

However, in the helium-fluorocarbon (He-FC) plasma treated sample there was a strong mass peak of  $F^-$  at 19 amu, as shown in Figure 8. It was

interesting to note that the intensity of the  $F^-$  peak was much higher, compared to other mass peaks, such as at 1 amu for  $H^-$ , at 12 amu for  $C^-$ , at 13 amu for  $CH^-$ , at 16 amu for  $O^-$ , and at 17 amu for  $OH^-$ . This indicates a breaking of different fluorocarbon species into smaller species, such as  $H^-$ ,  $C^-$ , and  $F^-$ , due to the bombardment of high energy gold primary ions during the SIMS testing. Other mass peaks also detected were at 31, 39, 43, 69, 79, 85, 93, 97, 103, 109, 113, 117, 119, 129, 131, 135, 141, and 143 amu, as shown in Figure 9, and also, a few similar molecules have been reported in the literature.<sup>14</sup> Among these, the 69 amu peak corresponds to  $CF_3^-$  and that at 119 amu to  $C_2F_5^-$ . The chemical structures of difluoro methane and pentafluoro ethane along with their possible fragmentation inside the helium plasma and the formation of various molecules are presented in Table 4. Together, Figure 9 and Table 4 indicate that in the plasma zone, both pentafluoro ethane and difluoro methane got fragmented into a number of smaller species and then, they reacted among themselves in different combinations, and mainly formed five types of hydrophobic molecules. These molecules might have reacted with cellulose, as the imparted hydrophobic finish was durable to even 30 washing cycles.

The ratio of various hydrophilic (oxygen containing species) to hydrophobic (carbon containing species) molecular species was calculated from the integer count of different mass peaks (Table 5). It can be seen that the  $O^-/C^-$  ratio is 3.72 in the untreated sample, which significantly decreases to 1.66 in the 12-min fluorocarbon plasma treated sample, i.e., a significant 55% decrease in the oxygen containing species (i.e.,  $-OH$  of cellulose).

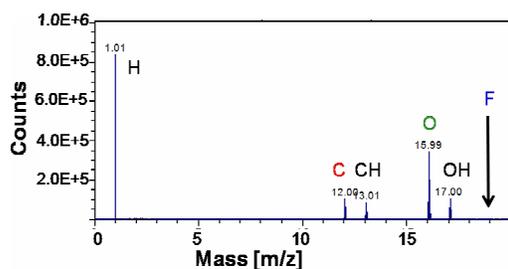


Figure 7: Negative ion mass spectrum of untreated sample

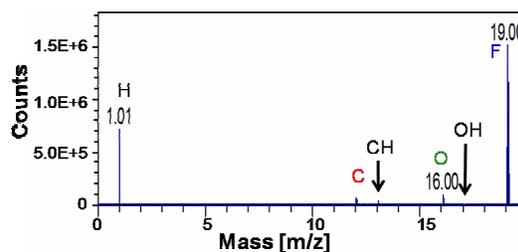


Figure 8: Negative ion mass spectrum of 12 min He-FC plasma treated sample

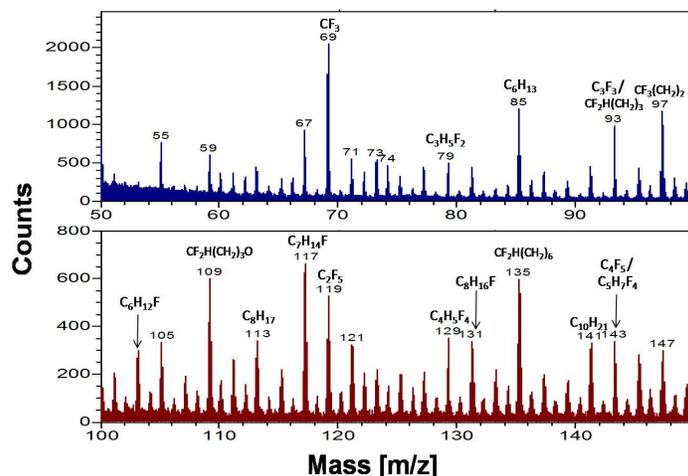


Figure 9: Higher molecular masses as detected by SIMS of 12-min He-FC plasma treated sample

Table 4

Fragmentation of fluorocarbon (FC) in helium plasma and formation of various hydrophobic molecules

$\begin{array}{c} \text{F} \\   \\ \text{F}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$ Difluoromethane	+	$\begin{array}{c} \text{F} & \text{F} \\   &   \\ \text{F}-\text{C} & -\text{C}-\text{H} \\   &   \\ \text{F} & \text{F} \end{array}$ Pentafluoroethane	$\xrightarrow[\text{Homolytic dissociation}]{\text{He plasma}}$	(a) $\cdot\text{F}$	(d) $\cdot\text{CF}$	(g) $\cdot\text{CHF}_2$
				(b) $\cdot\text{H}$	(e) $\cdot\text{CF}_2$	(h) $\cdot\text{CFT}_2$
				(c) $\cdot\text{CH}$	(f) $\cdot\text{CF}_3$	(i) $\cdot\text{CF}_2-\text{CF}_3$
Various fragments						
Sl. No.	Molecular weight	Chemical structures				
<b>A. Fluorocarbon molecules</b>						
(i)	31	$\cdot\text{CF}$				
(ii)	69	$\cdot\text{CF}_3$				
(iii)	119	$\text{CF}_3-\cdot\text{CF}_2$				
<b>B. Hydrocarbon molecules</b>						
(i)	85	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\cdot\text{CH}_2$				
(ii)	113	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\cdot\text{CH}_2$				
(iii)	141	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\cdot\text{CH}_2$				
<b>C. Hydrocarbon molecules with single fluorine atom</b>						
(i)	103	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\cdot\text{CHF}$				
(ii)	131	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\cdot\text{CHF}$				
<b>D. Alternative copolymer</b>						
(i)	79	$\text{CH}_3-\text{CF}_2-\cdot\text{CH}_2$				
(ii)	129	$\text{CH}_3-\text{CF}_2-\text{CH}_2-\cdot\text{CF}_2$				
(iii)	143	$\text{CH}_3-\text{CF}_2-\text{CH}_2-\text{CF}_2-\cdot\text{CH}_2$ Or $\cdot\text{C}_4\text{F}_5$				
<b>E. Other molecules</b>						
(i)	93	$\text{CHF}_2-\text{CH}_2-\text{CH}_2-\cdot\text{CH}_2$ Or $\text{CF}_2=\text{C}=\cdot\text{CF}$				
(ii)	135	$\text{CHF}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\cdot\text{CH}_2$				
(iii)	109	$\text{CHF}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\cdot\text{O}$				
(iv)	97	$\text{CF}_3-\text{CH}_2-\cdot\text{CH}_2$				

A similar result was seen in the  $\text{OH}^-/\text{CH}^-$  ratio. It was interesting to observe that the ratio of total hydrophilic species ( $\text{O}^-+\text{OH}^-$ ) to total hydrophobic species ( $\text{C}^-+\text{CH}^-$ ) decreased from 2.38 to 1.19 in the untreated to plasma treated

samples, which is again a 50% reduction in oxygen containing species.

The cotton cellulose became hydrophobic after plasma treatment due to the incorporation of various fluorocarbon and hydrocarbon molecules

in the cellulose, in addition to the removal of a large number of hydroxyl groups of cellulose. Additionally, the fluorine molecule might have also replaced the hydrogen atom and/or hydroxyl

group of cellulose, resulting in a decrease of  $H^-$ ,  $O^-$ , and  $OH^-$  peaks in the treated sample in comparison with the untreated sample.

Table 5  
Hydrophilic to hydrophobic molecular ratio obtained from mass spectra

Samples	$O^-/C^-$	$OH^-/CH^-$	$(O^- + OH^-)/(C^- + CH^-)$
Untreated	3.72	0.75	2.38
Plasma treated	1.66	0.46	1.19

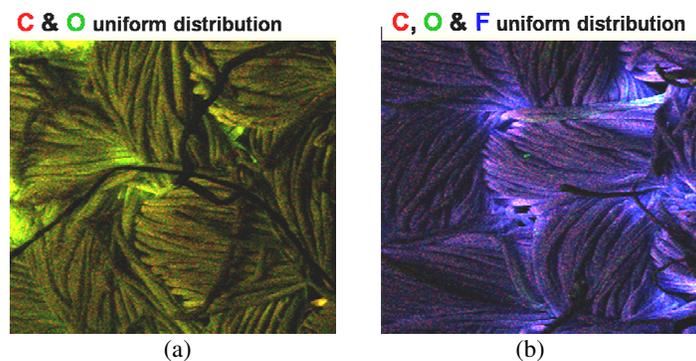


Figure 10: Chemical images of carbon (C), oxygen (O) and fluorine (F) molecules distribution in (a) untreated and (b) 12-min He-FC plasma treated cotton textiles (colour notation: red for  $C^-$  at 12 amu, green for  $O^-$  at 16 amu, and blue for  $F^-$  at 19 amu)

### Analysis of SIMS chemical images

SIMS chemical images were used to study the surface chemistry and distribution of the different molecules on the surface of both the untreated and the fluorocarbon plasma treated samples. From the negative mass ion spectra, three major mass peaks, such as  $C^-$  at 12 amu (red colour),  $O^-$  at 16 amu (green colour), and  $F^-$  at 19 amu (blue colour) were selected to study the distribution of these molecules on the surface of the samples. It can be seen from Figure 10 (a) that in the untreated sample  $C^-$  and  $O^-$  are uniformly distributed over the entire sample. The sample looks more greenish in colour due to the presence of a greater amount of oxygen, compared to that of carbon. This result corroborates what has already been observed by the mass spectrum analysis (Fig. 7).

On the other hand, the plasma treated sample (Fig. 10 (b)) mostly looks bluish in colour. This is due to the presence of a greater amount of  $F^-$  molecules on the surface of the plasma treated sample, compared to  $C^-$  and  $O^-$  molecules. A similar result has also been observed in the SIMS mass spectrum of the plasma treated sample, where the intensity of  $O^-$  and  $OH^-$  decreases profoundly. The  $F^-$ ,  $C^-$ , and  $O^-$  molecules are

found uniformly distributed over the entire surface area of the sample (Fig. 10). This implies that a uniform hydrophobic plasma reaction has happened on the cotton textile. Besides, individual fibres in the yarn structure, along with the typical twisted ribbon-like structure of the cotton fibres, are also visible in the plasma treated sample (Fig. 10 (b)). This is an indication of a nano-scale surface modification of the fibres and of the absence of any blockage of fibre-spacing by surface deposition. The untreated and the plasma treated samples look the same physically, but are significantly different chemically.

### CONCLUSION

Atmospheric pressure plasma was successfully generated in the presence of He and He-fluorocarbon (He-FC) gases and was used to impart water-repellent hydrophobic functionality in otherwise hydrophilic cotton textile. Optical emission spectra (OES) indicated the ionization of He and fragmentation of fluorocarbon gases. Fluorocarbon in the plasma zone showed the atomic lines of F at 429 nm, 357 nm, 341 nm, 325 nm, 311 nm and  $CF_2$  line at 318 nm. Helium was ionized with different patterns in pure He and helium-fluorocarbon (He-FC) mixture, thus

resulting differential ratios of various helium lines in these two plasmas. After the plasma reaction of He-FC, the cotton became highly hydrophobic. As a result of this, in the 3-min plasma treated sample, the water absorbency time increased to 9 min from 0.05 min (*i.e.*, 3 s) in the untreated sample. With increasing plasma treatment time, the degree of hydrophobicity was also found to increase and the 12-min plasma treated sample showed an excellent hydrophobic functionality with water absorbency time of >60 min and water contact angle of 142°, in contrast to ~0° for the untreated sample. The imparted hydrophobic finish was found to be durable to 30 home laundering cycles, and to storing at the ambient temperature for more than three months. Due to plasma reaction, different fluorine containing species, such as >C=CF<sub>2</sub>, –CF stretching, –CF<sub>2</sub> symmetric stretching, and –CF<sub>2</sub> asymmetric stretching, have been observed in the ATR-FTIR analysis. This is an indication of the plasma reaction of fluorocarbon fragments with the cotton cellulose. As a result, about 4.2% fluorine was also detected in the 12-min plasma treated sample during the EDX analysis. The SIMS result showed that not only fluorine is predominantly present on the surface of the plasma treated sample, but also it was uniformly distributed over the entire surface area. The fluorine rich moieties that were detected in SIMS were F<sup>-</sup>, CF<sub>3</sub><sup>-</sup>, and C<sub>2</sub>F<sub>5</sub><sup>-</sup>. The hydrophilic cotton textile became hydrophobic due to the reaction of various fluorocarbon and hydrocarbon molecules with cellulose. This signifies the fragmentation of the fluorocarbon precursor in the plasma zone and an *in-situ* reaction with the cellulosic textile. After the plasma reaction, though the sample became highly hydrophobic, no blockage of inter-fibre and intra-fibre spacing was found under SEM (physical image) and SIMS (molecular image), clearly suggesting this is a case of nano-scale surface modification of the textile. In the present study, the plasma processing of the textile was carried out in a dry state, without using water as a processing medium. It may be noted that a similar hydrophobic finishing of textiles by a

conventional method requires a significant amount of water, which also increases the pollution load and is a time-consuming process because of the requirement of post-drying the wet textile. On the other hand, atmospheric pressure plasma, which is an emerging technology, can be used beneficially to impart hydrophobic functionality to cellulosic textiles in a much shorter time and using no water.

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