

# Surface Characterization of Low Temperature Plasma-Induced Cashmere Fibre by Air Gas

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## Abstract

Low temperature plasma (LTP) processing technology was successfully applied to modify cashmere fibres and three kinds of assemblies were formed, i.e., weak-treated, optimised-treated and severe-treated ones. Treatment parameters were optimised in terms of the tensile behaviour, friction effect, wettability and touch feeling of cashmere without major modification of the properties inside the fibre. Detailed characterisation was performed to investigate the surface morphologies and chemical compositions of plasma-induced fibres. SEM demonstrates different minor etching effects of the treated cashmere fibres. XPS results indicate a significant increase in surface concentrations of O and N, and an obvious decrease in C after different LTP treatments as a whole. The C-H/C-C non-polar bonds were reduced and C-O/C-N, C=O polar groups were remarkably increased on the cashmere surface after plasma modification. In addition, a carboxyl group (O-C=O) formed. It is found that oxygen-containing bonds, namely, C-O/C-N, C=O and O-C=O, are responsible for the hydrophilic properties of cashmere.

**Key words:** plasma treatment, cashmere, SEM, XPS, surface, modification.

ment of relevant surface-related properties.

A shift toward highly functional and added-value textiles is now recognised as being essential to the sustainable growth of the textile industry [3]. Meanwhile maintenance of a cleaner environment has become one of the most vital global concerns. In recent years, efforts to modify cashmere in order to improve the properties have involved, besides chemical methods, procedures such as plasma treatment, thermal or ultra-sonication. LTP treatment is considered as an eco-friendly and sustainable technology, which has been widely used to modify the chemical and topographical properties of polymers and textiles surface [3-7], since the former involves high consumption and pollution of water resources. Furthermore plasma processing has the advantage of preserving the bulk properties as well as the touch of textiles owing to the nano-scaled surface modification of the substrate surface [8]. Literature abounds with works on the low temperature plasma treatment of textiles for different purposes [9-11], as an applicable alternative to chemical processes. Plasma treatments are known to induce physical and chemical surface changes in fibres via several concurrent processes [12, 13], such as activation, etching, grafting, cross-linking, etc. In the case of wool products, for example, LTP techniques with various gases, such as air, helium, nitrogen, oxygen, argon or their mixtures

[14, 15], have been used to improve wettability [6, 7, 16, 17], dyeing properties [6, 18-20], shrink resistance [21-23] and anti-pilling [24, 25] properties.

In the light of the obvious superiority of plasma processing, it is hardly surprising that lots of R&D centers and educational institutions have devoted considerable time and concerted effort to investigating the surface morphologies and chemical composition of plasma treated textiles [7, 12, 26-29]. However, only a few papers describe the effect of low temperature plasma treatments on cashmere [7], which is why continuation in the research is expected. In this work, we concentrate on the study of surface characterization of low temperature plasma-treated cashmere fibres with air gas. Since it is known that these processes may also cause undesired degradation, the plasma-treated specimens were divided into three categories, namely, weak treated, optimized treated and severe treated ones, in terms of tensile characteristics, the friction effect, wettability and touch feeling without changing their bulk properties. In particular, deep characterisation was performed to investigate the surface morphologies and chemical composition of plasma-treated fibre samples using SEM and XPS.

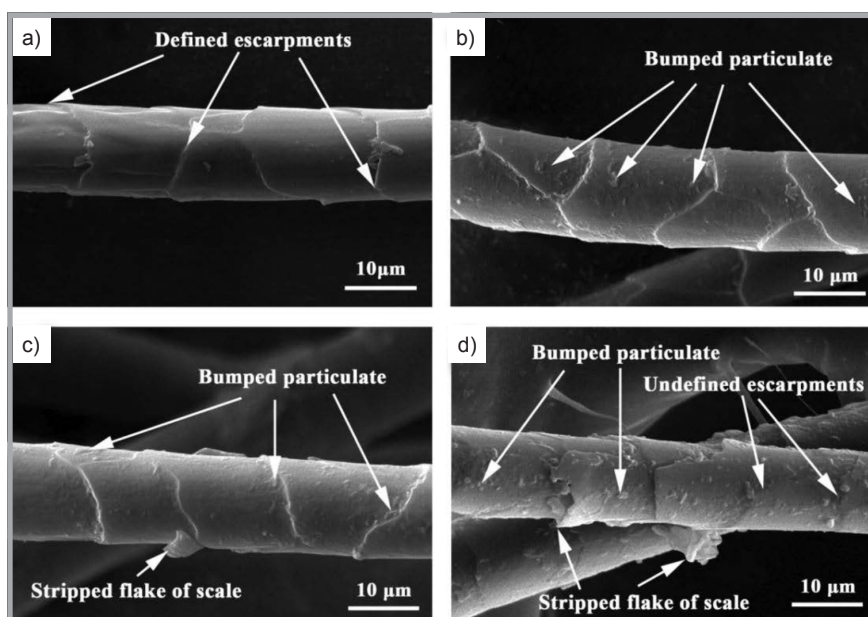
## Experimental

### Materials

Untreated cashmere fibres with a mean diameter of  $13.43 \pm 0.98 \mu\text{m}$  utilised in

## Introduction

Cashmere is a protein fibre consisting of two main components, namely, the cuticle and cortex. The cuticle is a layer of overlapping scales surrounding the cortex [1, 2]. The scale surface of cashmere fibres is inherently hydrophobic, and the scales need to be removed for improve-



**Figure 1.** SEM images of cashmere specimens: a) untreated fibre and b)-d) LTP treated.

this study were commercial materials (Ningxia Zhongyin Cashmere Co, Ltd; China). They were cleaned to remove any process additives such as oils, lubricants, and surfactants, etc. After this procedure, they were first dried with a centrifuge, and placed into a drying oven to be further dried. The staple length of fibres was 54 mm based on the hand-drawing method, and the content of oil and impurity of fibres were less than 1.5% and 2.0%, respectively. Note that a bundle of fibres was prepared and made parallel in a thin-web form to be plasma-modified uniformly.

#### Plasma processing with different treatment levels

All experiments were done on HD-1B Glow Discharge Plasma apparatus (Changzhou Shi-tai Plasma Technology Development Co, Ltd; China) with air gas. Cashmere fibres as prepared above were hung in the chamber of the device with different process conditions. According to our previous research, the control factors, including the cabinet pressure, discharge power and exposure time, were chosen. Tensile properties,

friction effect, wettability and touch feeling were selected as quality indicators. Finally three kinds of fibre samples, i.e., weak-treated (15 Pa, 100 W, 90 s), optimised-treated (10 Pa, 70 W, 150 s) and severe-treated (20 Pa, 100 W, 120 s), were obtained [30]. It should be noted that the specimens for capillary effect testing were formed in yarn styles made of 100% cashmere. All the tests were carried out under standard conditions of  $20\pm 2\%$  and  $65\pm 3\%$  RH.

#### Scanning electron microscopy (SEM)

The surface morphologies of treated and untreated cashmere fibres were observed by means of a KYKY-2800B SEM (Beijing KYKY Technology Co, Ltd; China) with 20 kV accelerated voltage at an 8-10 mm working distance. The samples were sputter gold coated under a vacuum prior to observation.

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

XPS was used to study the surface elemental composition and atomic ratios produced in the outermost layers of the fibre under different treatments. The fi-

bre specimens were analysed by means of ESCALAB MK-II (VG Scientific Ltd, UK) apparatus with an X-ray source. The base pressure in the chamber was controlled in the range of  $1.3\times 10^{-6}$  to  $1.3\times 10^{-7}$  Pa. The measurements were done at a normal emission angle. Survey scans were taken in the range 0-1000 eV and high resolution scans were obtained for the  $C_{1s}$  peak. Spectra were referenced to the hydrocarbon type  $C_{1s}$  component set at 285.0 eV. The spectra processing and fitting routines were done using XPS PEAK41 software developed by Chinese University of Hong Kong, China.

## Results and discussion

### Characteristics of plasma-treated specimens

The detailed characteristics of each plasma-treated sample are summarized in **Table 1**. Compared with the untreated fibre (a), the breaking force and elongation of cashmere samples (b-d) at various plasma-treated levels decreased slightly, and there are no major differences. For example, the loss of breaking force in the severe-treated one (d) is 10.15% compared with the untreated one (a). Both the static and dynamic friction effect show a decreasing trend, which is responsible for the enhancing of shrink-resistance. Also values of the capillary effect increase steadily with different treatment degrees.

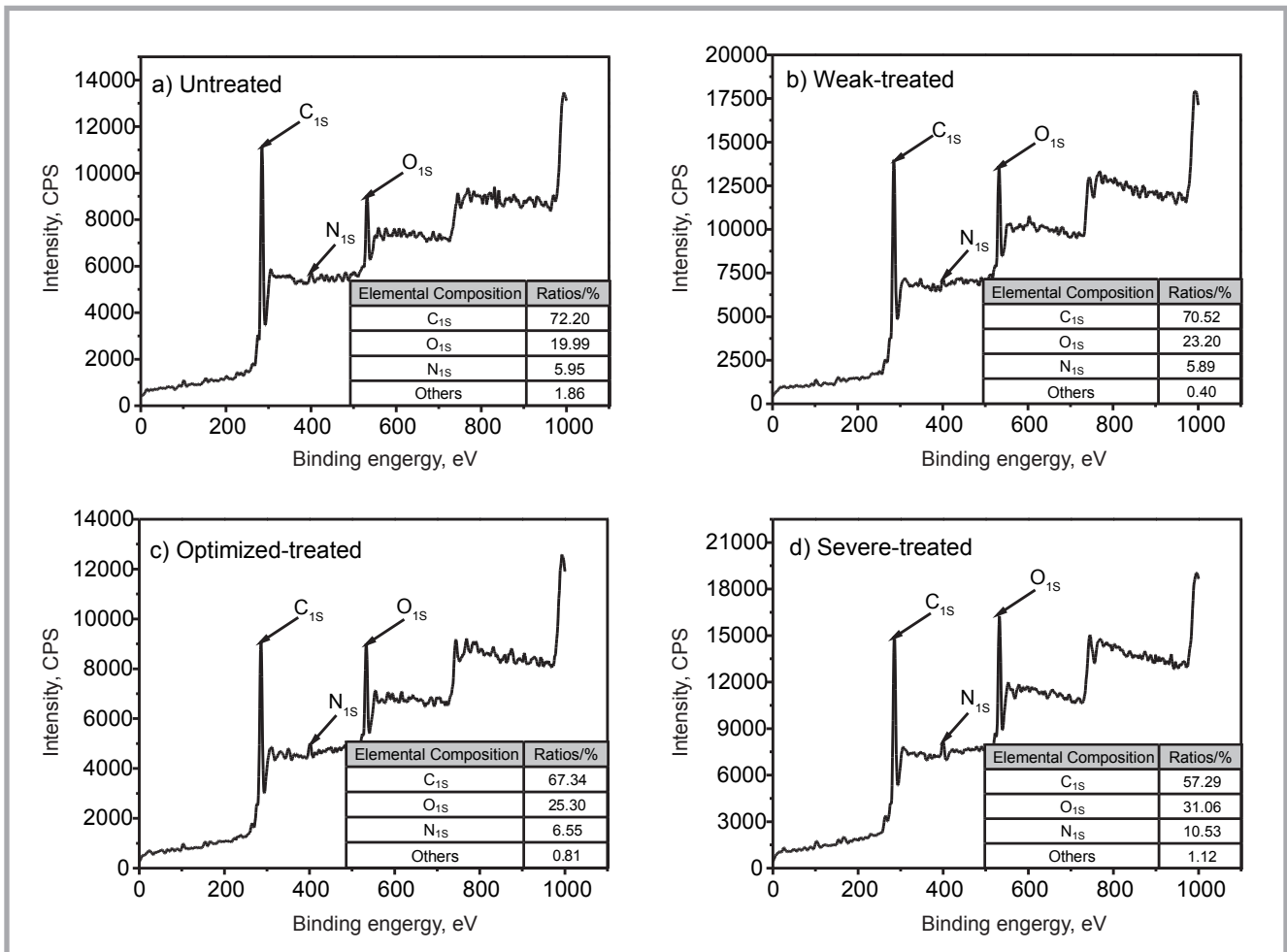
### Fibre surface morphology

Since the fibre surface plays an important role in the relevant behaviour, the effects of the treatment on the fibre surface have to be thoroughly investigated [19, 28]. SEM images of cashmeres both treated and untreated with LTP are shown in **Figure 1**.

The SEM micrograph of the untreated cashmere fibre clearly shows quite sharp scales and a smooth surface, as shown in **Figure 1.a**. The escarpments are prominent and well defined. On being subjected to air plasma treatment, the sharpness of fibre scales is reduced and the surface is rougher, which is also reported by literature [6, 26]. There is some change in the appearance when the fibre is exposed to weak plasma treatment (**Figure 1.b**), in which the scale edges are roughened and eroded, with some bumped particulate formed on the surface. In **Figure 1.c**, a moderate change in the fibre surface can be observed as the escarpments with roughened scale edges are lifted. Meanwhile the surface of the scale is stripped

**Table 1.** Detailed results of cashmere fibres with different plasma-treated levels.

Sample	Breaking force, cN	Elongation at break, %	Static friction effect, %	Dynamic friction effect, %	Values of capillary effect, cm
(a) Untreated	2.66	38.32	16.36	10.68	7.28
(b) Weak-treated	2.64	35.16	13.16	10.62	9.98
(c) Optimized-treated	2.56	34.17	13.09	10.55	10.34
(d) Severe-treated	2.39	36.05	9.79	7.19	11.30



**Figure 2.** XPS survey spectra of cashmere specimens with different plasma treatments.

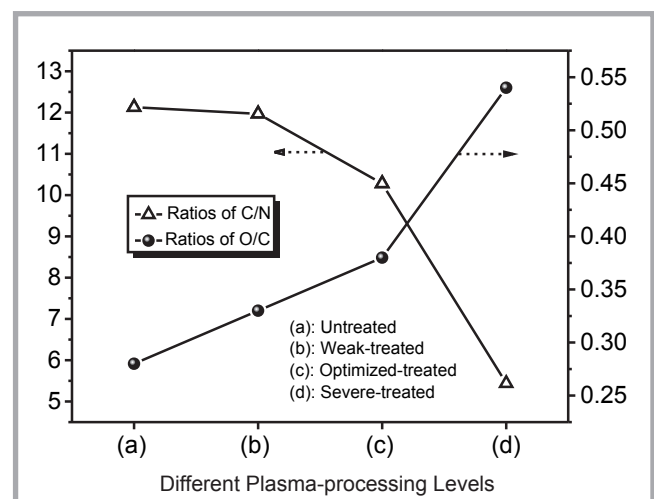
off or separated into flakes or some formation of particulate matter. Comparing **Figure 1.a, 1.b** and **1.c**, a slight reduction in scales thickness can be noticed in some areas, and no obvious defects or ruptures were observed. We can conclude that the plasma treatment can be considered as a non-destructive procedure [14]. The surface of fibres becomes appreciably different and the escarpments cannot be defined clearly with the severe LTP process, shown in **Figure 1.d**. The phenomenon observed above is attributed to the physical etching and chemical oxidation effects. None of these samples display burning or other deterioration after plasma treatment. However, treated samples appeared drier at touch-feeling, probably as a consequence of a partial dehydration owing to the plasma treatment. But the treated fibres can recover their original softness in a few days [7].

### XPS analysis

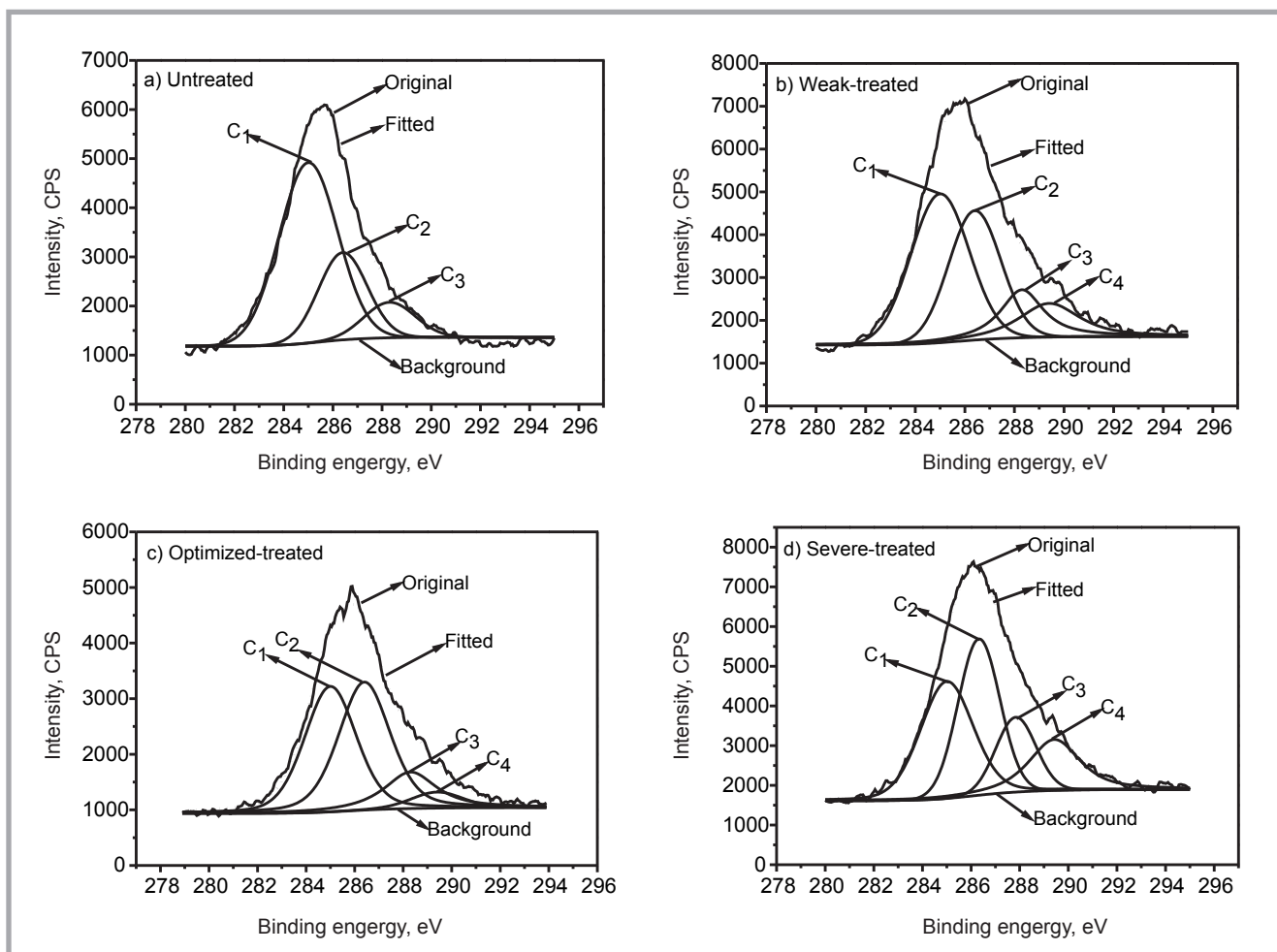
In order to understand the impact of plasma treatment on the chemical structure of cashmere fibres, XPS was used, which

also could provide quantitative and qualitative information about the chemical nature of external layers of the modified fibres [14, 28]. **Figure 2** presents wide-scan spectra obtained for the elements in cashmere. There are photoelectron peaks at binding energies of 533, 400 and 285 eV corresponding to O<sub>1s</sub>, N<sub>1s</sub> and C<sub>1s</sub>, respectively. Others here refer primarily

to elements S<sub>2p</sub> and P<sub>2p</sub>, etc. Additionally there are some weaker peaks in the range of 100-200 eV. On the whole, C<sub>1s</sub> decreased while O<sub>1s</sub> and N<sub>1s</sub> increased with different plasma processes, which is in agreement with that found previously [12, 27]. The C<sub>1s</sub> atomic concentration shows a 6.7% decrease from 72.2% (a) to 67.34% (c), while the O<sub>1s</sub> atomic con-



**Figure 3.** C/N and O/C ratios of cashmere specimens with different plasma-processing levels.



**Figure 4.** Curve fitted  $C_{1s}$  XPS spectra of cashmere with different plasma processes.

centration shows a 26.6% increase after optimised treatment compared with the untreated one.

C/N and O/C ratios of the different plasma-treated fibres are compared with those of untreated one in **Figure 3**. The C/N decreased and the O/C increased compared with the untreated cashmere. Protein fibres, such as wool, cashmere etc., show the presence of covalently bound lipids on the surface of their cuticle membrane. These are a complex mixture of polar and non-polar lipids, with long chain fatty acids being the predominant class [29]. The increase in the O/C ratio implies the etching of the external layer

of lipids and the insertion of oxygenated species onto the fibre surface. Both factors contributing together caused a change in the surface composition. Furthermore the C/N atomic ratio decreases significantly after severe treatment (d). The above-mentioned phenomenon may be explained by the fact that the reaction rate of the oxidation induced by atomic oxygen is much higher than that of the nitrification reaction induced by atomic nitrogen. The increase in the  $N_{1s}$  percentage can be also illustrated with the removal of the external hydrocarbon chains, which makes the underlying protein material more visible [7, 14, 29]. It must be noted that the  $N_{1s}$  content

increased dramatically after severe treatment, shown in **Figure 2.d**.

Herein, XPS PEAK41 software was used for thorough analysis of the surface structure of cashmere fibres and the chemical bond state after different plasma treatments. Shape evolutions of  $C_{1s}$  spectra of the specimens obtained using the Gaussian-Lorentzian curve-fitting method are reported in **Figure 4**, which provided interesting clues about the effect of the plasma/fibre interaction. According to literature [12, 28], in this paper,  $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$  were attributed to C-C/C-H (285.0 eV), C-O/C-N (286.4 eV), C = O (288.3 eV) and O-C = O (289.4 eV) functionalities, respectively. Furthermore the types of functional groups increase from three to four after plasma treatments.

Results of the fits are shown in **Table 2**. As can be seen, the most significant changes after plasma treatments are the decrease in the C-H/C-C component and formation of the new chemical bond O-C = O [12]. The C-O/C-N and C = O oxygen-containing groups increased

**Table 2.** Peak deconvolutions of  $C_{1s}$  spectra of modified cashmere fibre at different levels.

Samples	Relative peak areas, %				Peak area ratios		
	$C_1/285.0$ eV C-H/C-C	$C_2/286.4$ eV C-O/C-N	$C_3/288.3$ eV C=O	$C_4/289.4$ eV O-C=O	$C_2/C_1$	$C_3/C_1$	$C_4/C_1$
(a)	63.57	25.58	10.85	0.00	0.40	0.17	0.00
(b)	41.29	32.20	13.72	12.79	0.78	0.33	0.31
(c)	39.39	41.28	14.61	4.72	1.05	0.37	0.12
(d)	33.90	33.44	15.34	17.32	0.99	0.45	0.51

after the plasma processes. Only one bond (C-H/C-C) is responsible for the hydrophobic properties of untreated fibres, while three bonds (i.e., C-O/C-N, C=O and O-C=O) are polar and responsible for the hydrophilic properties of plasma-treated fibres. In particular,  $C_2/C_1$  and  $C_3/C_1$  peak area ratios prominently increased after optimized plasma treatment compared with the untreated one, from 0.40/0.17 to 1.05/0.37, respectively. Considering all the analysis above, the wettability of the cashmere surface can be enhanced with different plasma processing levels, primarily due to the mutual-interaction of etching and micro-oxygenation.

## Conclusions

Low-temperature plasma process-technology can effectively convert a hydrophobic cashmere surface into a hydrophilic one. Only minor etching effects were observed by characterisation with SEM. The C-H/C-C non-polar bonds were remarkably reduced and C-O/C-N, C=O & O-C=O polar groups were significantly increased on the cashmere surface at various plasma-processing levels. The C-H/C-C bond is responsible for the hydrophobic properties of untreated fibres, while the C-O/C-N, C=O and O-C=O bonds are responsible for hydrophilic properties of the plasma treated fibres. The results of this investigation helped to characterise the surface composition and determine the effect of LTP treatment on the surface properties of cashmere fibres. In the next step, we should combine gas mixtures and plasma-processing parameters to get a rather broad range of surface properties of the cashmere substrate. Furthermore as LTP tends to impair the handle of end-use products, plasma-treated, semi-finished products should be submitted to subsequent industrial treatments, such as softening, shrink finishing, etc.

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