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Characterization of hydro- and oleo-repellent pure cashmere and wool/nylon textiles obtained by atmospheric pressure plasma pre-treatment and coating with a fluorocarbon resin

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ABSTRACT

We describe the hydro- and oleo-repellent modification of pure cashmere and wool/nylon textiles by means of an atmospheric pressure plasma treatment followed by an impregnation with a fluorocarbon resin. Plasma treatments of both fabrics were realized with a dielectric barrier discharge (DBD) in humid air (air/water vapour mixtures), while the finishing process was performed in a foulard system, with an aqueous dispersion of a commercial fluorocarbon resin (FCR). A deep characterization allowed us to study the wettability, the surface morphologies and the chemical composition of the modified textiles. The chemical properties of the untreated and of the modified fabrics were investigated with X-ray photoelectron spectroscopy (XPS). SEM analyses coupled with a complete energy dispersive X-ray system (EDX) allowed us to investigate the distribution and the uniformity of the FCR on the fibres of the coated fabrics. Results show the importance of the plasma activation step to obtain a uniform coverage of the fibres with the FCR, which enhances the hydro- and the oleo-repellent properties of the modified fabrics.

1. Introduction

In recent years, there is a continuous demand of textile fabrics with specific surface properties, such as water and oil repellency, permanent hydrophilicity, printability, abrasion resistance, antibacterial properties, biocompatibility. In this respect, low temperature plasma treatment has been widely studied to modify the chemical and topographical properties of textiles [1]. The application of plasma technologies as a pretreatment or finishing process for textiles has become very popular because they are dry and eco-friendly processes, which changes only the outermost layer of the substrate without altering the bulk properties.

Literature abounds of works on low-pressure plasma treatments of textiles for different purposes, as an alternative to wet-chemical processes [1]. In particular, low-pressure plasma modification of textiles for hydro- and oleo-repellence (which are desirable in many applications) has been extensively studied in the past, with good results on different natural and synthetic fibres. However, despite its effectiveness, the inability to successfully incorporate low-pressure plasma treatment equipment into a continuous textile processing operation has limited the commercial viability of this technique.

In the last years, atmospheric pressure plasma treatments have gained considerable popularity for the surface modification of materials [1–4]. The main advantages over the low-pressure ones are the possibility to avoid the expensive vacuum systems, to decrease the time of treatment, and to simplify the technological transfer where the processes of production are making in continuous mode. As a matter of fact, the atmospheric pressure plasma treatment devices can be easily integrated with the continuous on-line processing of the textile materials. Recent literature focuses on atmospheric pressure plasma modification of textile by means of different plasma sources [5–12]. In particular, the plasma treatment with a dielectric barrier discharge (DBD) has been proved to be an efficient method for the enhancement of the wettability of different fabrics [5–7], while only few papers report the direct surface modification of textiles for hydro- and oleo-repellence by means of atmospheric pressure plasmas [13,14].

In a previous work [15], we employed a dielectric barrier discharge (DBD) in humid air (air/water vapour mixtures) for the plasma treatments of pure cashmere and wool/cashmere textiles, obtaining good results in terms of enhancement of the fabrics wettability and maintenance of the textile softness. Here, we describe the realization of hydro- and oleo-repellent pure cashmere and wool/nylon textiles by means of an atmospheric pressure plasma treatment followed by an impregnation with a fluorocarbon resin. Differently from many literature works, plasma modification of the fabrics was performed in conditions which could be transferred to the industrial on-line processing.

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Table 1
Operating parameters employed for the plasma treatment of the fabrics.

Power (W)	450
Speed of the mobile station (m/min)	2.5
Number of passes	4
Energy dose (W × min/m^2)	3600
Air flow (l/min)	10
Water vapour flow (g/h)	3

First of all, since the hydro- and oleo-repellent modification is a finishing process, we used fabrics which had been already dyed. Secondly, a set of plasma parameters which is useful also for the industrial world has been chosen. A deep characterization has been performed to study the wettability, the surface morphologies and the chemical composition of the modified textiles. In particular, SEM/EDX analysis allowed us to study the uniformity of the fluorocarbon resin on the fibres surface. Results show the importance of the plasma activation step to obtain a uniform coating of the fibres, which in turns gives an enhancement of the hydro- and the oleo-repellent properties of the modified fabrics.

2. Experimental

2.1. Materials

Commercial pure cashmere and wool/nylon fabrics were supplied by LoroPiana S.p.A. (Quarona, Italy) and used as received. Pure cashmere fabric had a grammage of 200 g/m^2. The second fabric had a grammage of 125 g/m^2 and was composed of wool fibres (weft, 60%$_{wt}$) and nylon fibres (warp, 40%$_{wt}$, fibre diameter ~10 μm). Since the aim of the work was the study of a finishing process to impart hydro repellent and oleo repellent properties to different textiles, we used fabrics which had been already dyed.

The commercial fluorocarbon polyurethane resin (FCR, Lamgard 48) employed for the impregnation of the plasma treated fabrics were supplied in aqueous dispersion by Lamberti S.p.A. (Gallarate, Italy).

2.2. Hydro- and oleo-repellent modifications of the fabrics

The DBD experimental device (S2V-2 corona station supplied by Tigres GmbH, Germany) has been extensively described elsewhere, and has been successfully employed for the enhancement of the wettability of different fabrics, with good retention of the originals touch and softness [15,16]. It consists of a stainless steel planar electrode coated with a poly(tetrafluoroethylene) sheet (thickness = 1 mm), where textile samples to treat are placed on. Two rod electrodes (220 mm long, 8 mm diameter), coated with pure (>99.7%) syntherized Al_2O_3 dielectric (thickness 2 mm), are mounted on a mobile station, at a distance of 20 mm from each other. The two rods are connected through an HV cable to the secondary coil of a transformer, whose primary circuit is connected to a power generator, operating at 45 kHz and providing the driving high voltage for the discharge. The distance between the plate electrode and the rod electrodes could be varied from 0.5 mm to few millimeters. In our experiments it is fixed at 2 mm. During the treatments, the station can move horizontally with a speed that can be varied between 0.7 and 7 m/min. The electrical power supplied to the discharge could be varied up to a maximum of 450 W. For each treatment, the energy density, or dose, could be estimated by: $D = Pn/vl$, where P is the electrical power, v is the speed of rod electrodes, l is their length and n is the numbers of passes over the specimens.

The plasma treatments of the fabrics were performed in humid air (air/water vapour mixtures).

Based on previous experience [15], we selected process parameters which allowed an effective hydrophilic modification without fabrics deterioration. These parameters are shown in Table 1. In particular, we chose a speed of the mobile station (2.5 m/min) and a number of passes (4) which are a compromise between the necessity of avoiding a fabric damaging and the will of adopting a set of parameters which could be also useful for practical industrial applications.

The inlet fluxes are controlled by a gas/vapour mixing system. The air flow is regulated using a mass flow controller (El-flow by Bronkhorst). To introduce water vapour in the gas flow, we employed a liquid flow controller with an evaporator/mixer system (Bronkhorst CEM System). The inlet fluxes are injected between the high voltage electrodes through an injection flute that ensures uniform fluxes on the whole length of the electrodes.

Untreated and plasma treated fabrics were impregnated with an aqueous dispersion (concentration of 25 g/l) of a commercial fluorocarbon resin in a foulard system and dried in an oven at 140 °C for 2 min.

2.3. Characterization techniques

2.3.1. Wettability measurements

Water contact angles (WCAs) were measured with 3 μl deionized water droplet on a Dataphysics OCA 20 (Dataphysics) instrument at room temperature. After deposition of the drop on the textile sample, the contact angle was measured within 1 min. All the contact angles were determined by averaging the values obtained at 10 different points on each sample surface.

Table 2
Composition of the solutions employed in the 3M standard test for water repellency.

Number of the test liquid	Composition of the test liquid	Surface tension at 20 °C (dynes/cm)
0	Water	72.8
1	90/10 water/isopropyl alcohol	42.0
2	80/20 water/isopropyl alcohol	33.0
3	70/30 water/isopropyl alcohol	27.5
4	60/40 water/isopropyl alcohol	25.4
5	50/50 water/isopropyl alcohol	24.5
6	40/60 water/isopropyl alcohol	24.0
7	30/70 water/isopropyl alcohol	23.7
8	20/80 water/isopropyl alcohol	23.3
9	10/90 water/isopropyl alcohol	22.4
10	Isopropyl alcohol	21.7

Table 3
Liquids employed in the standard test for oleorepellency.

Number of the test liquid	Composition of the test liquid
1	Kaydol mineral oil
2	65/35 Kaydol/n-hexadecane
3	n-Hexadecane
4	n-Tetradecane
5	n-Dodecane
6	n-Decane
7	n-Octane
8	n-Eptane

Table 4
Atomic percentage of elements measured by XPS on untreated and differently modified pure cashmere and wool/nylon fabrics.

Sample	Atomic composition (%)					O/C	F/C
	C	O	N	S	F		
Untreated pure cashmere	74.4	14.2	9.0	2.6	0	0.19	0
Pure cashmere + plasma	69.9	19.4	9.3	2.4	0	0.28	0
Pure cashmere + plasma + FCR	62.0	9.4	6.3	1.9	20.4	0.15	0.33
Untreated wool/nylon (wool)	77.4	10.7	8.6	3.3	0	0.14	0
Untreated wool/nylon (nylon)	70.6	15.7	13.7	0	0	0.22	0
Nylon/cashmere + plasma + FCR (wool)	63.3	8.5	4.5	1.6	22.1	0.13	0.35
Nylon/cashmere + plasma + FCR (nylon)	66.0	11.0	7.6	0	15.4	0.16	0.24