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Innovative Hybrid Fluorocarbon Coating on UV/Ozone Surface Modified Wool Substrate

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Abstract: In an attempt to enhance the desired properties of textile substrates, hybrid fluorocarbon coating of the wool substrate together with UV/O_3 treatment was investigated. The application of fluorocarbons on the wool fabrics was found to have some processing problems due to the chemistry and structure of the wool fiber surface. Therefore, in this research, the use of UV/Ozone as a promising and environmentally friendly fast treatment for the surface modification of the wool substrate was studied. Both-sided UV/Ozone irradiation, in comparison to only one-sided UV/Ozone irradiation, resulted in the slightly better performance as evaluated for both pad-dry-cure and print-dry-cure fluorocarbon finishing treatments. By this novel hybrid finishing, the fabric outside finished with the fluorochemical exhibited hydrophobicity with 3M water repellency of 10 and the fabric inner side, which was in contact with the human body, kept its natural desirable moisture absorption. The UV/Ozone pre-treatment, by oxidizing the topmost layer of the fibers surface, imparted better durability of the fluorocarbon treatment to repeated washings and abrasion. However, UV/Ozone irradiation process could not overcome the drawback of fluorocarbon molecules reorientation after washing and/or abrasion, but the samples retrieved their hydrophobicity after hot-pressing. Overall, after the application of this novel method (both-sided UV/Ozone modified and then fluorochemical finish treated via the print-dry-cure process) on wool fabric, the inner side of the wool fabric, which was next to the skin, could provide desirable comforting moisture absorption for human body and protect the human skin from the negative hydrophobic effects of fluorocarbon chains; moreover, the outer side of the wool fabric exhibited highly durable (to repeated washings and abrasion) water and oil repellency properties to the outside world, helping the wool fabric display better dimensional stability with less shrinkage performance after repeated washings and higher air-permeability performance without detrimental effects on the tensile properties.

Keywords: Wool, UV/Ozone, Fluorocarbon, Hybrid finishing, Surface modification, Repellency

Introduction

Surface modification of textile materials and polymers is extremely important from a practical point of view. Among various traditional and new technologies used for surface treatments of textiles and polymers, the UV/Ozone irradiation, as an alternative to gas plasma treatment, is a powerful tool not only for fulfilling the environmental necessities, but also for imparting very specific functions such as improved wettability, adhesion, adsorption, printability, chemical reactivity, and light sensitivity [1,2]. Indeed, employing ultraviolet (UV) light in the presence of ozone (UVO) as a surface treatment (oxidation) is a fast, inexpensive, and environmentally benign process requiring only ultraviolet light and ozone [3]. Good oxidative efficiency can be achieved by coupling UV radiation and ozone. By UV/Ozone treatment, surface molecules are excited and/or dissociated by the absorption of 253.7 nm radiation. The 253.7 nm radiation is also absorbed by ozone, and this is partly responsible for the destruction of ozone to atomic oxygen and subsequently, the oxidation of the excited molecules in the surface to form volatile molecules desorbed from the surface [2,4]. As a result of this, the surface energy could be increased due to the introduction photo-oxidized polar groups on the surface [2]. The UV treatment mainly affects the properties of surface region with minimal influence on the bulk properties, depending on the choice of UV lamp and optical geometry [5]. Recently, the effect of UV irradiation on the possibility of the low temperature dyeing of wool and its associated chemical and physical changes on wool was investigated. The UV-treated fabrics were characterized in terms of morphological, chemical, and physical properties by SEM, FTIR-ATR spectra, water contact angle measurements, bursting and pilling test. In this research, wool fabrics were treated by two different intensity of UV irradiation, 50 and 900 mW/cm^2, for 5 min and 40 s, respectively. The authors concluded that the UV treatment can reduce the dyeing temperature of acid dyes on wool for more than 20 ^{o}C with good color levelness and wash fastness without deterioration of the wool physical properties [6]. The same research group also published a paper in which reported that the morphological properties of wool would not be changed by the UV treatment but its surface tension is changed due to the increase of the hydroxyl group on the wool surface, confirmed by FTIR examination. They, also, showed that the possibility of having a dyed fabric by the same shade but in different depth or a fabric with two different shades in each fabric side. The authors concluded that these effects are obtained due to the "The increased affinity through structural modifications of the wool cuticle by UV rays" [7].

On the other hand, easy-care garments with better performance

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have recently attracted much attention throughout the textile industry. The application of fluorocarbon finishes to textiles offers water, oil, soil repellency, and soil release. It is a key chemical finish performance indicator for the textile marketing.

Hybrid finishing is a combination of different process types which enhance the performance of textile materials, thereby leading to new desired properties. The combination of contrasting effects on one textile material can improve its functional properties. In this paper, a new procedure was investigated for wool fabric in order to combine water repellent and oil-soil repellent in addition to the moisture transport effect.

It is generally essential for wool fabric to modify the wool fiber surface using a suitable treatment in order to obtain acceptable dimensional stability, good color strength, levelness, and brightness performance during dyeing and/or printing. It should also create proper surface adhesion with adequate wettability properties [1,2,8]. The use of many previously widely applied chemical processing methods such as chlorination was confined due to strict environmental legislations related to absorbable organohalogens (AOX). Therefore, recent works have been focused on the development of dry treatments with low or zero effluent. Moreover, UV/Ozone irradiation method does not lead to damage by heat to the fabrics since this modification is carried out under mild thermal conditions or low application temperatures, leading to a suitable wool fabric pre-treatment process [9]. Therefore, in this research, the application of UV/Ozone as a promising and environmentally friendly treatment for surface modification of wool substrate was investigated in an attempt to increase wear comfort via hybrid finishing using a fluorochemical, thereby leading to better moisture management. It must be noted that in the conventional garment, generally the multilayer technology is applied with a textile layer having the required repellent properties with moisture transporting as another layer. Unfortunately, this combination leads to an increase in weight, wear comfort reduction, and distinctly restricted breathability. Therefore, this novel hybrid finishing could possibly be the potential treatment to solve these drawbacks in such a way that the face of the fabric would be finished with a fluorochemical having the acceptable fastness properties, while the inner side of the fabric would keep its natural moisture absorption in a desirable manner.

Experimental

Materials

Standard wool fabric botany serge (100 % wool fiber, 200 g/m^2) was supplied by Whaleys Ltd, Bradford. The selected fluorocarbon (Evo Protect FXM) is of C_8 fluorochemicals with Laundry Air Dry, LAD, effect which generally used for all textile fibers and their blends, and non-ionic detergent (Sera Wet C-NR) were supplied by DyStar. Other chemicals were of analytic grade from Merck, Germany.

Fabric Preparation

The wool fabric was first scoured to eliminate any possible impurities which would adversely affect the surface finishing. This was done by 1 m*l*/*l* detergent and 0.2 g/*l* sodium carbonate (for pH 8-9) with a liquor ratio of 30:1 at 40 ^{o}C for 30 min. Then, all samples were rinsed for 15 min and then air dried without any tension.

UV/Ozone Treatment

The scoured samples were treated with UV/O_3 source which consists of a UV chamber, an oxygen concentrator and an ozone generator. The operation was carried out in the UV chamber which comprised of five parallel UV lamps, Philips TUV 11 W mercury vapor, 253.7 nm UV radiation, fixed horizontally at the top of the box. The wool fabric was placed under the lamps, with an exposure distance of 1 cm between sample and UV lamps. With the association of the oxygen concentrator (7f-3a, Lencen china), the ozone generator (Cog-2a, Arda, France), produced ozone which flowed into the UV chamber. In an earlier studies, 20 min of UV/Ozone treatment on wool fabric was reported to result in the best surface modification performance for wool fiber with instant wettability as well as minimum physical and chemical damages on the bulk properties of the wool fiber [10,11]. For that reason, in this study, the exposure time of UV/Ozone irradiation on the wool fabric was chosen to be 20 min for each side of the fabric. Only one side of the fabric and also, both sides were irradiated by UV/Ozone for 20 min in order to compare the effects of one-sided and double-sided UV/Ozone treatment on different performance properties of wool fabrics. Also, an unmodified wool fabric was brought to the study to serve as control for comparison. Immediately after the irradiation process, the wool samples were washed again to remove any possible debris and/or etched species formed by the aforementioned method. This was followed by a warm and cold rinse and then finally air dried without any tension.

Fluorochemical Treatment

The scoured and surface modified, via UV/Ozone treatment, wool fabrics were fluorocarbon finished by two different methods. Fluorochemical finish via these both methods was applied on all three types of wool fabrics, as mentioned in the above ‘UV/Ozone treatment’ section (only one-side UV/Ozone modified wool fabric; both-side UV/Ozone modified wool fabric; and the unmodified control wool fabric).

In the first method (pad-dry-cure), the wool fabric was impregnated by padding in a treatment bath containing 75 g/*l* fluorochemical, acetic acid as a pH adjuster (5-6), and 5 m*l*/*l* 2-propanol, as a volatile wetting agent. Subsequently, the wool samples were passed through a two-roll laboratory padder (Mathis, Switzerland) at a 100 % wet pick-up. As it is known, both sides of the wool fabric were finished with impregnation finishing bath via the pad application process.

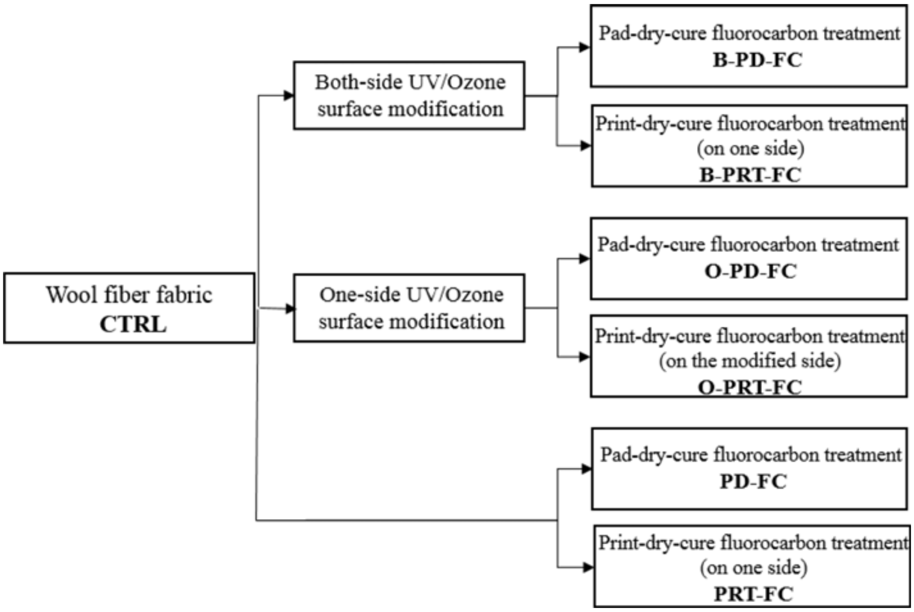

Figure 1. The procedure of the treatments and abbreviation.

However, in the second method (print-dry-cure), in order to finish only one side of the wool fabric with hydrophobic fluorochemical, the irradiated side of the wool samples was coated via open screen printing only. The finishing paste contained 75 g/*l* fluorochemical, acetic acid as the pH adjuster (5-6) and 2 % thickener agent. As indicated, in this second method, unlike the first method, only one side of the wool fabric was coated via the printing process.

Both impregnated (the first method) and coated (the second method) wool fabrics were then dried at 100 °C for 5 min, and then cured at 150 °C for 4 min using a Warner Mathis AG lab type dryer (Niederhasli/Zurich). The schematic procedure of the treatments and related abbreviations are illustrated in Figure 1.

Fabric Evaluation Methods

Fabric performance and mechanical properties after the respective treatments and laundering were examined. Wash and abrasion fastness assessment, 3M water and oil repellency tests, wettability, dimensional stability evaluation, tensile strength, and air permeability measurements were carried out for all treated wool fabric samples.

Water and Oil Repellency Testing

The modified and fluorochemical treated samples were tested for oil and water repellency according to the 3M tests [12,13] after the initial treatment as finished, abrasion, 1st, 3rd, and 5th washing cycles. Standard test liquids are shown in Tables 1 and 2.

After laundering, as explained below, the finished wool samples were hot-pressed using an Elna Press (SDL) with a temperature set for wool fabrics in order to evaluate the effect of reorientation of fluorocarbon polymer chains on the wool fiber and consequently, to determine the final water

Table 1. Standard test liquids for water repellency test [12]

Composition of test liquid	Water repellency rating number
Water	W
90/10 Water/2-Propanol	1
80/20 Water/2-Propanol	2
70/30 Water/2-Propanol	3
60/40 Water/2-Propanol	4
50/50 Water/2-Propanol	5
40/60 Water/2-Propanol	6
30/70 Water/2-Propanol	7
20/80 Water/2-Propanol	8
10/90 Water/2-Propanol	9
2-Propanol	10

Table 2. Standard test liquids for oil repellency test [13]

Composition of test liquid	Oil repellency rating number
Liquid Parafin	1
65/35 liquid paraffin/ n-hexadecane by volume at 21 °C	2
n-hexadecane	3
n-tetradecane	4
n-dodecane	5
n-decane	6
n-octane	7
n-heptane	8

and oil repellency of the finished wool samples after a hot-press application following repeated washings.

Laundering

The laundering cycles were carried out on both modified and then treated and control wool fabrics using a Wascator FOM 71 MP Lab Washer-Extractor washing machine, with standard program 5A. The procedure adopted conformed to British Standard EN ISO 6330 (Domestic Washing and Drying Procedures for Textiles Testing). In each washing cycle, 30 g of non-phosphate ECE reference detergent (without optical brightening agent) was used. All fabrics were washed individually to eliminate the risk of cross contamination.

Abrasion Test

Abrasion fastness of the finished samples was tested by a Martindale Wear & Abrasion tester in accordance with ASTM D4966-89 test method. Hydrophobicity property was measured via 3M water and oil repellency tests after the abrasion test in order to evaluate the flourochemical abrasion resistance on the wool fabrics. Fluorocarbon chemically treated, abraded unmodified and modified wool fabrics were hot-pressed using an Elna Press (SDL), as done in after washing, in order to examine the effect of hot pressing on oil/water repellency properties of the abraded fabrics.

Wettability

Wetting properties of wool samples were evaluated according to AATCC Test Method 79-1992 after conditioning each sample to reach equilibrium in a standard atmosphere having a relative humidity of 65±2 % at 21±1 ^{o}C. At least 10 drops of distilled water were applied on different parts of the fabric samples and the average time of their absorbency was reported as wetting time in s.

Dimensional Stability

Fabric squares with the size of 0.1 m×0.1 m were marked with reference points 0.02 m from the edge; then they were put completely relaxed in water containing 1 g/*l* Sera Wet C-NR with the liquor ratio of 50:1, at 40 ^{o}C for 60 min. The wet distances between these points were measured as an initial area in order to evaluate the relaxation shrinkage. The samples shrinkage was evaluated after different washing cycles. Subsequent to each wash, the weft and warp shrinkages were measured at three positions and area shrinkage was considered for the dimensional stability, samples were kept for other experiments.

Tensile Strength Test

The tensile properties (stress and strain) of the modified and then treated and control wool fabrics were determined. An Instron 5564 tensile testing machine was employed, and the procedure was followed as prescribed by the BS 13934-1:1999 Standard test method with a gauge length of 0.1 m and the crosshead speed of 0.050 m/min. The average value of 10 measurements for each wool sample was reported.

Air Permeability

The air permeability was evaluated according to BS 9237-1995 using the conditioned samples. The test surface area was 5.07 cm^2, and the pressure drop was 100 Pascal. In this experiment, the air permeability, R, in mm/s, was calculated using equation (1) [14].

$$R = qv/A \times 167 \tag{1}$$

where qv is the arithmetic mean flow rate of air, in dm^3/min (*l*/min); 167 is the conversion factor from dm^3/min·cm^2 to mm/s; and A is the area of fabric under test (in cm^2).

Results and Discussion

Wettability of UV/Ozone Modified Wool Fabrics

Table 3 exhibits the wettability performance of the unmodified and UV/Ozone modified wool fabrics before the fluorochemical finishing treatment. The wetting time of the unmodified wool fabric was more than 300 s. Actually, this was expected, since, as known, wool fibers are naturally slightly hydrophobic [8,15]. The topmost surface layer of wool fiber is thought to have a covalently bounded lipid layer responsible for epicuticle layers' hydrophobic nature [16].

On the other hand, in the case of UV/Ozone modified wool fabrics, the wetting time was less than 1 s (Table 3). The significantly better hydrophilicity performance of these UV/Ozone modified wool fabrics, in comparison to the unmodified control wool fabrics, could be explained by the oxidation of surface disulfide linkages on the wool fiber, leading to more presence of hydrophilic groups on the fiber surface along with the volatilization of the surface lipids during UV/Ozone irradiation process, which eventually resulted in increased interface polarity and fiber wettability [2,17]. Indeed, such modification on the outer epicuticle and exocuticle of wool fiber improves its wettability and wool coloration performance [16]. A closer look at UV/Ozone treatment by El-Zaher showed that the surface molecules of the wool fibers were excited or dissociated by the absorption

Table 3. Effect of UV/O$_3$ treatment on wettability time of wool fabrics

Wool sample[a]		Wetting time (s)
Unmodified		>300
One-side modified	Modified side	<1
	Unmodified side	>300
Both-sides modified		<1

[a] Surface modification by UV/Ozone irradiation was carried out either on only one side of the wool fabric or on both sides of the wool fabric.

of short wavelength UV radiation in a photosensitized oxidation process that resulted in an extensive surface modification at the outer epicuticle and exocuticle layers of wool fibers; this, in turn, led to the formation of cystic acid and free radicals species and the oxidation of disulfide bonds [9].

The wool fiber surface contained many different lipid components which were covalently bound to the fiber surface, such as 18-methyleicosanoic acid (18-MEA) (as a major component), C_{16}-C_{20} fatty acid thioester derivatives as well as similarly sized fatty acid ester species [17]. These surface lipids of the wool fiber were modified or volatilized [18], and/or removed by UV/Ozone treatment, especially the C_{21} fatty acid [19] and the 18-methyleicosanoic acid (18-MEA) ones [17].

Also, Table 3 clearly indicates the great difference between the wetting time of face and the back of the one-side irradiated sample (less than 1 s versus more than 300 s, respectively).

Actually, this demonstrates that UV/Ozone treatment on only one side of the fabric was limited to the surface of this side of the wool fabric, leading to hybrid functional fabrics with two different properties, one on each side of the wool fabric, such as different degrees of wettability. In other words, two different properties, one on each side of the wool fabric, can be generated via this one-sided single irradiation process.

Water and Oil Repellency Performance and Their Fastness

3M water and oil repellency of the UV/Ozone modified and unmodified samples are illustrated in Tables 4 and 5.

CTRL wool fabrics exhibited 3M water repellency of 2 and 3M oil repellency of 0, before and after washing (Tables 4 and 5). Similarly, the uncoated side of the PRT-FC wool fabric and the uncoated side of O-PRT-FC wool fabric behaved exactly the same, by 3M water repellency of 2 and 3M oil repellency of 0 (Tables 4 and 5). The tested sides of these both wool fabrics did not receive any fluorochemical treatment, thereby leading to the same behavior of the CTRL wool fabrics. This again showed that UV/Ozone treatment performance could mainly be limited only to the applied surface side of the wool fabric as experienced in the wettability results.

However, the uncoated side of B-PRT-FC wool fabric resulted in 0 for both 3M water and oil repellency, before and after washing and hot-pressing. This observed water repellency difference (2 versus 0, 3M water repellency) between these samples could be related to the different wettability performance of those wool fabrics (Table 3). Indeed, the hydrophobic nature of the unmodified wool (more than 300 s, Table 3) led to 3M water repellency of 2 before and after washing and/or hot pressing (Table 4). Uncoated both-side UV/Ozone modified exhibited less than 1 s for wettability (Table 3), thereby leading to 3M water repellency of 0 before and after washing and/or hot-pressing (Table 4).

In addition, fluorocarbon finishing led to the maximum oil and water repellency, with 3M water repellency of 10 and oil repellency of 8 for the fluorochemical finished sides of fabrics either by pad or printing method before any washing (Tables 4 and 5). As can be seen in Tables 4 and 5, such quite high water and oil repellency performances of fluorocarbon treated fabrics with both methods were diminished after the first wash. After the third wash, this trend did not stop. Eventually, after the 5th wash, the lowest water and oil repellency performances were observed for both methods.

Table 4. 3M water repellency results of UV/O_3 modified and then fluorocarbon treated wool fabrics before and after repeated washing cycles and hot-pressing

Fluorochemical treatment	Pre-treatment (UV/O_3 surface modification)		Before wash	Before hot-pressing			After hot-pressing		
				After 1 wash	After 3 washes	After 5 washes	After 1 wash	After 3 washes	After 5 washes
Untreated	Unmodified (CTRL)		2	2	2	2	2	2	2
Pad-dry-cure	Unmodified (PD-FC)		10	3	2	1	8	6	3
	One-side modified (O-PD-FC)	Modified side	10	8	6	3	10	10	7
		Unmodified side	10	6	4	2	7	7	5
	Both-sides modified (B-PD-FC)		10	9	7	5	10	10	10
Print-dry-cure	Unmodified (PRT-FC)	Coated side	10	2	1	1	8	6	2
		Uncoated side	2	2	2	2	2	2	2
	One-side modified (O-PRT-FC)	Coated side[a]	10	6	4	2	10	10	6
		Uncoated side[b]	2	2	2	1	2	2	2
	Both-sides modified (B-PRT-FC)	Coated side	10	5	5	2	10	9	8
		Uncoated side	0	0	0	0	0	0	0

[a]Coating via printing was applied on the UV/Ozone treated side of the wool fabric and [b]uncoated side did not receive UV/Ozone treatment. As indicated on [a], the other side of the fabric received UV/Ozone irradiation.

Table 5. 3M oil repellency results of UV/O_3 modified and then fluorocarbon treated wool fabrics before and after repeated washing cycles and hot-pressing

Fluorochemical treatment	Pre-treatment (UV/O_3 surface modification)		Before wash	Before hot-pressing			After hot-pressing		
				After 1 wash	After 3 washes	After 5 washes	After 1 wash	After 3 washes	After 5 washes
Untreated	Unmodified (CTRL)		0	0	0	0	0	0	0
Pad-dry-cure	Unmodified (PD-FC)		8	1	0	0	6	4	1
	One-side modified (O-PD-FC)	Modified side	8	6	4	1	8	8	5
		Unmodified side	8	4	2	0	5	5	3
	Both-sides modified (B-PD-FC)		8	7	5	3	8	8	8
Print-dry-cure	Un-odified (PRT-FC)	Coated side	8	0	0	0	6	4	0
		Uncoated side	0	0	0	0	0	0	0
	One-side modified (O-PRT-FC)	Coated side[a]	8	4	2	0	8	8	4
		Uncoated side[b]	0	0	0	0	0	0	0
	Both-sides modified (B-PRT-FC)	Coated side	8	3	3	0	8	7	6
		Uncoated side	0	0	0	0	0	0	0

[a]Coating via printing was applied on the UV/Ozone treated side of the wool fabric and [b]uncoated side did not receive UV/Ozone treatment. As indicated on [a], the other side of the fabric received UV/Ozone irradiation.

Therefore, repeated laundering led to a loss of both oil and water repellency performance of fluorocarbon finish treated wool fabrics with two different methods due to the surface reorientation and lack of enough wash fastness of the fluorocarbon segments in the finish [20,21].

Since macromolecules determine their conformations according to the immediate neighboring phase, surface properties of these polymers in the air are different from those in the water. The rotational and diffusional migration of hydrophobic moieties away from the water/polymer interface would cause the decay of the hydrophobicity when the treated sample is immersed in water [22]. The B-PD-FC sample exhibited better water (3M=5) and oil (3M=3) repellency even after 5 washes in comparison to other fabrics. Other processed fabrics, apart from controls, led to a range of 1-3 water repellency and a range of 0-1 oil repellency after 5 washings.

After washing, the reorientation of Evo Protect FXM during air-drying was incomplete and both water and oil repellencies were clearly decreased. This observation could be actually proved by hot-pressing process application. It is clear from Tables 4 and 5 that subsequent hot-pressing following room temperature air drying restored most of the original water and oil repellency performance for fluorocarbon finish treated wool fabrics with two different methods. This was due to the dual action of fluorochemicals that resulted from the reorientation of hydrophobic chains during hot-pressing. It must be noted that the decay of the repellency after wet treatment was partially due to the removal of the hydrophobic moieties, because they retrieved their original repellency performance after heating at $120\,^{\circ}\mathrm{C}$. So, migrations of hydrophobic moieties caused by the water were at least partially reversible. The buried fluorine-containing moieties migrated toward the surface on heat treatment [22]. So, UV/Ozone irradiation process could not overcome the drawback of fluorocarbon molecules reorientation after washing on the wool fabric. This means that hot-pressing process is still needed to retrieve the effective water and oil repellency properties back on UV/Ozone modified wool fabric finished with fluorochemical.

After repeated washings and/or hot-pressing, UV/Ozone irradiated and then fluorocarbon treated wool fabric exhibited better water and oil repellency performance in comparison to fluorocarbon treated wool fabric (without receiving precursor surface modification via UV/Ozone irradiation) (Tables 4 and 5). Indeed, a lower reduction in the 3M properties was observed by the surface modification of the UV/Ozone treatment. For example, PD-FC sample exhibited 8, 6, 3 for water repellency after washings and hot-pressing and 6, 4, 1 for oil repellency after washings and hot-pressing; on the other hand, modified side of O-PD-FC sample showed 10, 10, 7 for water repellency after washings and hot-pressing and 8, 8, 5 for oil repellency after washings and hot-pressing (Tables 4 and 5).

Another striking example showing the visible effect of UV/Ozone treatment alone on repellency performance of wool fabric is the comparison of modified and unmodified side of O-PD-FC sample; 10, 10, 7 versus 7, 7, 5 for water repellency and 8, 8, 5 versus 5, 5, 3 for oil repellency, after washings and hot-pressing (Tables 4 and 5). Similar examples can be also given for print-dry-cure method too (Tables 4 and 5). It seems that better penetration and attachment of fluorocarbon segments take place on the wool fiber surface after the modification by UV/Ozone irradiation.

Both pad-dry-cure and print-dry-cure finishing applying methods resulted in very close, comparable and even almost similar repellency performances for both water and oil, after washing and hot-pressing (Tables 4 and 5).

However, all UV/Ozone irradiated and fluorocarbon finished wool fabric samples exhibited quite high water and oil repellency after repeated washings and hot-pressing; overall, the best water and oil repellency performance was observed for B-PD-FC sample, leading to 10, 10, and 10 maximum points available for water repellency and 8, 8, and 8 for oil repellency after repeated washings and hot-pressing (Tables 4 and 5). But one should not forget that after pad-dry-cure process, one-sided UV/Ozone modified (O-PD-FC) and both-sided UV/Ozone modified (B-PD-FC) wool samples exhibited quite high water and oil repellency performance for both sides of the wool fabric.

On the other hand, the achieved effects obtained on both-sided UV/Ozone modified and then flourochemical finish applied by the print-dry-cure method were actually very interesting. This is since, via this method, only one side of the wool fabric is coated with fluorocarbon polymers, leading to quite high water (10, 9, 8; after washings and hot-pressing) and oil (8, 7, 6; after washings and hot-pressing) repellency for that printed side of the fabric. In contrast, the uncoated side (during the use of the print-dry-cure method) of B-PRT-FC sample was still hydrophilic with less than 1 s for wetting and exhibited 0 for water repellency and again 0 for oil repellency (Tables 4 and 5). Actually, by using this novel method, the wool fabric inner side, which was in contact with the human body, kept its natural desirable moisture absorption; therefore, the negative hydrophobic effects of fluorocarbon on human skin could be minimized. The sessile water droplets on the different hydrophobic samples are shown in Figure 2.

Abrasion Fastness

3M water and oil repellency before and after abrasion test can be seen in Table 6. Again, after abrasion, as experienced after repeated washings, the reorientation of the fluorochemical chains caused the reduction in water and oil repellency, which was partially retrievable again after hot-pressing (Table 6). The positive effect of hot-pressing, which was previously explained in detail, could be again quite visible after the abrasion for wool fabrics (Table 6). This subsequent hot-pressing again restored most of the original water and oil repellency performance for fluorocarbon finish treated wool fabrics prepared via both finishing methods. The decay of hydrophobicity for the UV/Ozone modified sample was less than that of the unmodified comparable samples after abrasion and hot-pressing. For example, B-PD-FC and PD-FC samples exhibited 3M water repellency of 7, 10 versus 2, 6 and 3M oil repellency of 5, 8 versus 0, 4 for, respectively. Again, as observed in repeated washings, it can be inferred that better penetration and attachment of fluorocarbon segments take place on the wool fiber surface after the modification by UV/Ozone irradiation, thereby leading to creating better surface interface for the covalent bonding of the finishing agent on the wool fiber surface against washing and abrasion.

The reduction of hydrophobicity performance after abrasion,

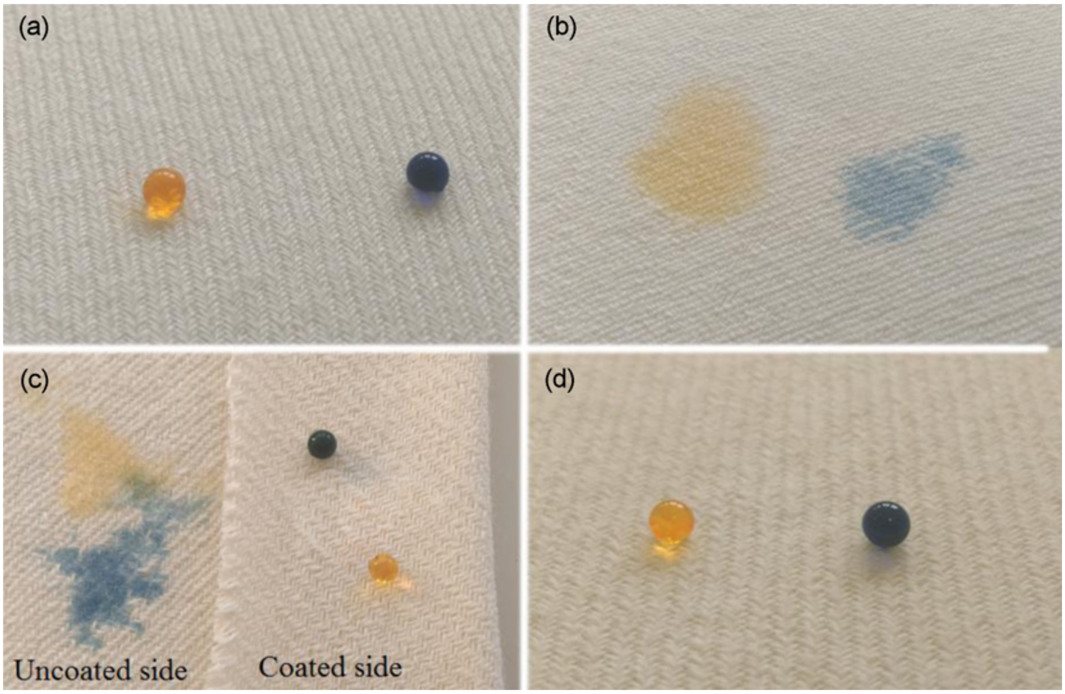

Figure 2. The sessile water droplets on the (a) PD-FC, (b) UV/ozone treatment applied, (c) B-PRT-FC, and (d) B-PD-FC fabrics.

Table 6. 3M water and oil repellency results of UV/O_3 modified and then fluorocarbon treated wool fabrics before and after abrasion and hot-pressing

Fluorochemical treatment	Pre-treatment (UV/O_3 surface modification)	Water repellency			Oil repellency		
		Before abrasion	After abrasion		Before abrasion	After abrasion	
			Before hot-pressing	After hot-pressing		Before hot-pressing	After hot-pressing
Untreated	Unmodified (CTRL)	2	1	1	2	1	1
Pad-dry-cure	Unmodified (PD-FC)	10	2	6	8	0	4
	One-side modified (O-PD-FC)	10	3	8	8	1	6
	Both-sides modified (B-PD-FC)	10	7	10	8	5	8
Print-dry-cure[a]	Unmodified (PRT-FC)	10	2	8	8	0	6
	One-side modified (O-PRT-FC)	10	5	10	8	3	8
	Both-sides modified (B-PRT-FC)	10	6	10	8	4	8

[a] Coating via printing was applied on the UV/Ozone treated side of the wool fabric. Repellency performance before and after abrasion and hot-pressing were measured on the coated side of the wool fabric.

but before hot-pressing for the both-sided modified samples prepared by both finishing application methods was less than that for the one-side UV/Ozone modified ones. A similar evaluation can be conducted for the ones finished with the pad-dry-cure method, even after hot-pressing (Table 6).

After hot-pressing, both-sided UV/Ozone modified, B-PD-FC and B-PRT-FC samples, retrieved the original maximum levels of water (10 each) and oil (8 each) repellency properties (Table 6).

Dimensional Stability of Wool Fabrics

Dimensional stability is one of the most important characteristic for wool fabrics application since wool fabrics can shrink in the vicinity of the moisture or during wash [23,24]. Area shrinkage properties of UV/O_3 modified, as a pretreatment, and then fluorocarbon treated wool fabrics are shown in Table 7. CTRL wool fabric exhibited 6.7 %, 12.6 %, and 38.5 % shrinkage after 1, 3, and 5 washes, respectively; on the other hand, fluorocarbon treated, by both application methods, both modified and unmodified, by UV/Ozone irradiation, wool samples displayed lower shrinkage (Table 7).

Moreover, according to Table 7, there was an increase in the shrink-proofing property of the wool fabrics after a UV/Ozone treatment, thereby leading to significantly lower shrinkage results. Indeed, as an example, PD-FC sample displayed 4.0 %, 7.9 %, and 24.3 % shrinkage after 1, 3, and 5 washes, respectively; on the other hand, similarly finished O-PD-FC and B-PD-FC samples exhibited 1.0 %, 4.9 %, and 9.8 % shrinkage and 0 %, 2.0 %, and 4.9 % shrinkage after 1, 3, and 5 washes, respectively (Table 7). So, as it can be easily seen from shrinkage results that both-sided UV/Ozone treatment led to better dimensional stability with less shrinkage rates in comparison to one-sided UV/Ozone treatment. Indeed, the fluorocarbon treated samples which received both-sided UV/Ozone irradiation showed the lowest shrinkage rates amongst all studied wool samples. Here, the mechanism of shrink-proofing was based on the degradation method, which was the softening of the scales and subsequently, the reduction of directional friction effect, DFE, due to the oxidation process. It is worth mentioning that both fluorocarbon application methods (pad-dry-cure and print-dry-cure) exhibited similar shrinkage rates for both-sided UV/Ozone irradiated wool samples, before and after repeated washing cycles.

Table 7. Area shrinkage of UV/O_3 modified and then fluorocarbon treated wool fabrics before and after repeated washing cycles

Fluorochemical treatment	Pre-treatment (UV/O_3 surface modification)	Area shrinkage (%)		
		After 1 wash	After 3 washes	After 5 washes
Untreated	Unmodified (CTRL)	6.7	12.6	38.5
Pad-dry-cure	Unmodified (PD-FC)	4.0	7.9	24.3
	One-side modified (O-PD-FC)	1.0	4.9	9.8
	Both-sides modified (B-PD-FC)	0	2.0	4.9
Print-dry-cure	Unmodified (PRT-FC)	4.9	9.8	25.2
	One-side modified (O-PRT-FC)	1.0	4.9	11.6
	Both-sides modified (B-PRT-FC)	0	2.0	5.9

Table 8. Effect of UV/O_3 treatment on tensile stress and strain properties of wool fabrics*

Wool sample[a]	Strain[b] (%)	Stress[b] (N/mm^2)
Unmodified	22.7±2.5	8.0±0.9
One-side modified	27.2±9.1	8.8±0.6
Both-sides modified	27.8±6.2	9.3±0.6

[a]Surface modification by UV/Ozone irradiation was carried out either on only one side of the wool fabric or on both sides of the wool fabric. *Error is calculated in 95 % confidence interval.

Tensile Properties of UV/Ozone Modified Wool Fabrics

The effect of UV/O_3 treatment on the tensile (stress and strain) properties of wool fabrics is shown in Table 8.

A quick look at Table 8 shows that there are slight differences for both strain and stress properties of the wool samples. This very slight increase was observed on tensile stress after 20 min of UV/Ozone irradiation, some thing which is actually in line with the earlier findings [9,16].

This slight tensile stress increase after the UV/Ozone irradiation might be due to the dominance of crosslinking reactions over the chain scission during these stages and the increasing amount of crosslinked macromolecules [9]. However, after a closer look, these slight tensile stress differences could be regarded as statistically insignificant. Therefore, unmodified, one-sided modified and both-sided modified, via UV/Ozone irradiation, wool fabrics exhibited close, comparable tensile properties.

It can be seen from Table 8 that UV/Ozone irradiation did not lead to any adverse and/or detrimental effect on the tensile (stress and strain) properties of wool fabrics. As earlier experienced from wettability and repellency results, this imply that UV/Ozone irradiation on one-side and/or both-sides of the fabric could be counted as a surface finish, without any significant effects on the bulk properties [25,26].

Air Permeability

Air permeation properties of UV/O_3 modified, as a pre-treatment, and then fluorocarbon treated wool fabrics are shown on Table 9. CTRLwool fabric exhibited the air permeation value of 216.4±3.6 m*l*/s·cm^2 (Table 9). PD-FC and PRT-FC (*no UV/Ozone treatment*) wool fabrics resulted in 213.4±5.7 m*l*/s·cm^2 and 208.1±4.3 m*l*/s·cm^2, respectively (Table 9). So, fluorocarbon treatment alone slightly decreased the air permeability of the wool fabric.

One-sided UV/Ozone irradiation improved the air permeability property of the wool fabric by 233.4±4.9 over 213.4±5.7 for fluorocarbon finished samples via pad-dry-cure (O-PD-FC) and around 213.9±2.1 over 208.1±4.3 fluorocarbon finished samples via print-dry-cure methods (O-PRT-FC). According to the statistical difference between the results of the fabric permeability to air, it can be concluded that UV/Ozone treatment makes the fabrics more permeable to the air, probably due to the oxidation of the wool fiber surface and possible slight size reduction of fibers diameter. Both-sided UV/Ozone irradiation led to even more air permeability than one-sided modified ones and unmodified controls studied (Table 9). Overall, UV/Ozone surface irradiation again led to some other positive performance improvement, which was on air permeability this time, on wool fabrics.

Table 9. Air permeation of UV/O_3 modified and then fluorocarbon treated wool fabrics*

Fluorochemical treatment	Pre-treatment (UV/O_3 surface modification)	Air permeation (m*l*/s·cm^2)
Untreated	Unmodified (CTRL)	216.4±3.6
Pad-dry-cure	Unmodified (PD-FC)	213.4±5.7
	One-side modified (O-PD-FC)	233.4±4.9
	Both-sides modified (B-PD-FC)	242.0±3.9
Print-dry-cure	Unmodified (PRT-FC)	208.1±4.3
	One-side modified (O-PRT-FC)	213.9±2.1
	Both-sides modified (B-PRT-FC)	223.3±7.8

*Error is calculated in 95 % confidence interval.

Conclusion

This research focused on the application of UV/Ozone irradiation as an environmentally friendly treatment for the surface modification of wool substrate. It was applied as a pre-treatment modification prior to fluorochemical finishing process. UV/Ozone modified wool fabrics exhibited significantly better hydrophilicity performance (less than 1 s versus more than 300 s) in comparison to the unmodified control wool fabric. UV/Ozone treatment on only one side of the fabric was limited to the surface of this side of the wool fabric, leading to hybrid functional fabrics with two different properties on each side of the fabric, such as different degrees of wettability. Fluorocarbon finishing resulted in the maximum oil and water repellency with 3M water repellency of 10 and the oil repellency of 8 for the fluorochemical finished sides of fabrics, either by pad or the printing method before any washing. A lower reduction in the 3M properties was observed by the surface modification of the UV/Ozone treatment after abrasion and/or washings. Both pad-dry-cure and print-dry-cure finishing applying methods resulted in very close, comparable and even almost similar repellency performances for both water and oil after hot-pressing. On the other hand, the achieved effects on both-sided UV/Ozone modified and flourochemical finish applied wool fabrics by the print-dry-cure method were actually very interesting and promising. Actually, by the application of this novel method, the wool fabrics inner side, which was in contact with the human body, kept its natural desirable moisture absorption and therefore, the negative hydrophobic effects of fluorocarbon for human skin could be minimized. There was also an increase in the dimensional stability property of the wool fabrics after an UV/Ozone treatment, leading to significantly lower shrinkage results. UV/Ozone irradiation did not lead to any adverse and/or detrimental effect on the tensile (stress and strain) properties of wool fabrics and made the fabrics more permeable to the air.

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References

1. M. N. Micheal and N. A. El-Zaher, *J. Appl. Polym. Sci.*, **90**, 3668 (2003).
2. J. Shao, C. J. Hawkyard, and C. M. Carr, *J. Soc. Dyers Colour.*, **113**, 126 (1997).
3. J. R. Vig, *JVST A*, **3**, 1027 (1985).
4. T. Clark, J. D. Ruiz, H. Fan, C. J. Brinker, B. I. Swanson, and A. N. Parikh, *Chem. Mat.*, **12**, 3879 (2000).
5. K. R. Millington, *Color. Technol.*, **116**, 266 (2000).
6. M. Periolatto, F. Ferrero, and G Migliavacca, *J. Text. Inst.*, **105**, 1058 (2014).
7. G. Migliavacca, F. Ferrero, and M. Periolatto, *Color. Technol.*, **130**, 327 (2014).
8. J. Xin, R. Zhu, J. Hua, and J. Shen, *Color. Technol.*, **118**, 169 (2002).
9. N. El-Zaher and M. Micheal, *J. Appl. Polym. Sci.*, **85**, 1469 (2002).
10. P. Davari-Dolat Abadi, M. S. Dissertation, Isfahan University of Technology, Isfahan, 2012.
11. F. Fattahi, H. Izadan, and A. Khoddami, *Prog. Color Colorants Coat.*, **5**, 15 (2012).
12. Z. Mazrouei-Sebdani, A. Khoddami, and S. Mallakpour, *Colloid. Polym. Sci.*, **289**, 1035 (2011).
13. Z. Mazrouei-Sebdani and A. Khoddami, *Prog. Org. Coat.*, **72**, 638 (2011).
14. A. Khoddami, M. I. Soleimani, and H. Gong, *Text. Res. J.*, **81**, 2006 (2011).
15. A. Khoddami, H. Gong, and G. Ghadimi, *Fiber. Polym.*, **13**, 28 (2012).
16. E. M. Osman, M. N. Michael, and H. Gohar, *Int. J. Chem.*, **2**, 28 (2010).
17. J. Mall, P. Sims, and C. Carr, *J. Text. Inst.*, **93**, 43 (2002).
18. J. Dyer and A. Grosvenor, *Natural Dyes,* 111 (2011).
19. J. Shao, C. Carr, C. Rowlands, and J. Walton, *J. Text. Inst.*, **90**, 459 (1999).
20. S. Arunyadej, R. Mitchell, J. Walton, and C. M. Carr, *J. Text. Inst.*, **89**, 696 (1998).
21. F. Audenaert, H. Lens, D. Rolly, and P. Vander Elst, *J. Text. Inst.*, **90**, 76 (1999).
22. T. Yasuda, T. Okuno, K. Yoshida, and H. Yasuda, *J. Polym. Sci. Pt. B-Polym. Phys.*, **26**, 1781 (1988).
23. P. Jovanĉić, D. Jocić, R. Molina, M. R. Juliá, and P. Erra, *Text. Res. J.*, **71**, 948 (2001).
24. A. Khoddami, F. Ghahremanzadeh, and C. M. Carr, *Fiber. Polym.*, **11**, 1170 (2010).
25. M. Michael, N. El-Zaher, and S. Ibrahim, *Polym.-Plast. Technol. Eng.*, **43**, 1041 (2004).
26. A. Wan and W. Yu, *Text. Res. J.*, **82**, 27 (2012).