Water-repellent cotton fabrics by ultraviolet curing and plasma treatment

WATER-REPELLENT COTTON FABRICS BY ULTRAVIOLET CURING AND PLASMA TREATMENT

Claudia Udrescu, Monica Periolatto, Franco Ferrero
Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
franco.ferrero@polito.it; claudia.udrescu@polito.it

ABSTRACT
Cotton fabrics were finished by radical ultraviolet (UV) curing or plasma polymerization of perfluoro-alkyl-polyacrylates. These products are water dispersions indicated for thermal application, but thermal crosslinking involves high temperatures (150°C), whereas UV-curing or plasma treatment is carried out at low temperature. Polymer add-on of 3% and 5% o.w.f. were investigated in order to obtain water-repellency without lost of fabric handling.
The surface properties of treated and untreated textiles were tested by optical measurements of the contact angle of water on the textile surface. The same measurements were made on samples subjected to repeated washings to test wash fastness of the finish treatment. Finished fabric samples were characterized with DSC, FTIR-ATR and XPS analyses. Finally, moisture adsorption and water vapor permeability were determined.

KEY WORD
Water-repellency; fabrics; cotton; UV-curing; plasma.

INTRODUCTION

Water and oil-repellency is currently conferred to cotton by thermal polymerization of perfluoro-alkyl-polyacrylate resins, which enable a strong increase of water and oil contact angles on the treated fabrics [1]. Usually fluorochemicals are available as aqueous emulsions and are applied to fabrics by pad-dry-cure method. Then the padded fabric are dried in air at 80-100°C and subsequently cured at 150–175°C in hot flue for some minutes.
In our previous works [2-3] cotton fabrics were water-repellent finished by UV-curing of silicone and urethane acrylates, epoxy-silicone and fluorinated resins. The results of contact angle, wettability and moisture adsorption showed that water- repellency is significant already at low resin add-on.
The advantages of UV-curing are well known: energy saving (low temperature process), low environmental impact (no solvent emissions), simple, cheap and small equipment, high treatment speed. These aspects make the UV-curing method highly competitive with thermal polymerization.
Alternatively, plasma polymerization of fluorinated resins can be carried out on padded fabrics and results similar to those obtained with thermal or UV-curing can be expected. Plasma polymerization can be conducted in a low pressure batch reactor in nitrogen atmosphere since oxygen interferes with radical reactions. The main advantage of plasma polymerization consists on surface modification of the fibers without affecting the bulk properties [4-6]. The treatment is carried out at low temperature avoiding a possible damage due to thermal degradation. Moreover the process results environment-friendly without solvent or greenhouse gas emissions.
In the present work cotton fabrics were finished by radical UV-curing or plasma polymerization of commercial perfluoro-acrylates usually cured with thermal treatment and the results were compared. The surface properties of treated textiles were tested by optical measurements of the water contact angle and the same measurements were made on samples subjected to repeated washings to test wash fastness of the finish treatment. Moreover DSC, FTIR-ATR and XPS analyses were also performed, while moisture adsorption and vapor permeability measurements were determined to characterize the treated fabric performances.

APPROACH

Materials

The used fabric was plain-weave pure cotton (144 g/m^2) previously washed but not subjected to any finishing process. This material presents a 0° contact angle with water, since the drops are soon adsorbed owing to the great hydrophilicity of cotton.
Repellan® EPF and NFC, by Pulcra Chemicals and Oleophobol® CP-C by Huntsman, commercial finishes for thermal application, based on perfluoro-acrylic copolymers, were used. These resins are water dispersions, whose solid content was determined about 17%. For what concern UV-curing, Darocure 1173 (2-hydroxy-2-methyl-1-phenylpropan-1-one) from Ciba Specialty Chemicals was added as a radical photo-initiator.

Thermal polymerization

To achieve a homogeneous spread of the liquid resin on cotton, the emulsion was diluted with water and applied

onto the surface of 5x2.5 cm^2 fabric strips then dried in an oven at 100°C for 15 min. The amount of resin put on the fabrics was adjusted according to the desired weight percentage and the emulsion concentration. Add-on of 3% and 5% o.w.f. were usually investigated in order to obtain the desired properties without loss of fabric handling.
According to the technical sheets, thermal polymerization was achieved in 2-3 min at 140-150°C for Repellan and in 3 min at 150°C for Oleophobol.

UV-curing
For UV-curing, the formulation was first prepared by dissolving the required ratios of resin and photoinitiator (2% w/w of the solid resin content), then the emulsion was applied onto fabric strips and dried as in the case of thermal treatment. The surface coated fabrics were exposed to UV radiation using a medium-pressure mercury lamp with a light intensity on the fabric of about 20 mW/cm^2, in a small box equipped with a quartz window under nitrogen atmosphere (oxygen content lower than 20 ppm). The required radiation dose was obtained adjusting the distance of textile from the lamp and the exposition time. An exposure time of just 40 seconds was necessary to obtain a solid film.

Plasma polymerization
For plasma polymerization experiments, a small laboratory batch reactor (Plasmod by March Instruments Inc.) was utilised. A low pressure (1.3 mbar) nitrogen plasma was applied at 50 W for 30 s to fabric samples previously impregnated by finish emulsion and dried.

Weight gain and gel content evaluation
The weight gain of cotton, that is the add-on of polymer, was calculated as in Eq (1):

$$Weight\ gain\ (\%) = \frac{w - w_0}{w_0} \times 100 \qquad (1)$$

where w is the weight of treated cotton and w_0 the weight of original cotton fabric previously dried in air oven at 100°C for 15 min.
Resin emulsion is adsorbed by textiles, so the polymerized structure does not form a film onto the fabric surface, but penetrate inside the cotton fibers. To test if thermal treatment or UV-curing or plasma polymerization was effective even inside the fabric, the amount of polymerized resin was evaluated by gel content determination. This was calculated by measuring the residual weight after 24 h of extraction with chloroform on the cured fabrics, at room temperature, followed by solvent evaporation in oven at 90°C for 1 h. Gel content can be considered a true polymerization yield, because the unpolymerized resin is removed by the solvent.

Contact angle measurements
The surface properties of coated and uncoated textiles were tested with optical measurements of static contact angle of water drops on the textile surface. The measuring liquids was HPLC grade water. The contact angle values should be as higher as the hydrophobic behavior of textile is greater. The measurements were carried out on a Krüss DSA 10 instrument, equipped with a video camera, and the contact angles were estimated by the instrument software according to the fitting method that uses Young-Laplace equation.

Water-repellency fastness to washings
On cotton samples finished with Repellan or Oleophobol, water-repellency fastness to domestic washing was evaluated according to UNI-EN ISO 105-C01. Each sample was treated in a sealed test tube with a solution of 5 g/L of ECE detergent maintaining a fabric to bath mass ratio of 1:50. The tubes were fixed on oscillating plane plunged in a thermostatic bath at 40°C and agitated for 30 min. Finally the samples were rinsed in cold water and dried in air oven at 60°C. Each sample was subjected to the same treatment five times and contact angle measured before and after washing.

Water vapor permeability
The determination of the water vapor permeability of finished fabrics was evaluated according to ASTM E96, procedure B (shallow cup filled with water) at 23°C and 50% relative humidity. As a result, there was a flux of vapor through the fabric, which became constant when stationary conditions were established. The system was maintained under the same conditions for 3 days. Once a day the flask was weighed, to evaluate the vapor amount which effectively crossed the fabric. The water vapor transmission rate is defined in eq. (2):

$$WVTR = \frac{W}{A \cdot t} \qquad (2)$$

where $WVTR$ = water vapor transmission rate [$g \cdot m^{-2} \cdot d^{-1}$], W = penetrating mass [g], A = crossed surface [m^2] and t = time, in days [d].

DSC, FTIR-ATR and XPS analyses
DSC analyses were carried out by a Mettler TA 3000 Calorimeter equipped with a Mod. 20 DSC cell. Samples of about 5 mg of yarn were sealed in the standard aluminum pans of 40 µl and submitted to DSC analysis in the range from 50 to 400°C at the heating rate of 10 °C/min under nitrogen flux. The data were processed on a personal computer with the aid of the Star SW 9.10 software. FTIR-ATR analyses were performed on a Nicolet FTIR 5700 spectrophotometer equipped with a Smart Orbit ATR single bounce accessory mounting a diamond crystal. Each spectrum was collected directly on single yarn by cumulating 128

scans, at 4 cm^{-1} resolution and gain 8, in the wavelength range 4000-600 cm^{-1}.

X-Ray photoelectron spectra (XPS) were performed with a PHI 5000 Versa Probe system (Physical Electronics, MN, U.S.A.) using a monochromatic Al radiation at 1486.6 eV, 25.6 W power, with an x-ray beam diameter of 100 μm. The energy resolution was about 0.5 eV. XPS measurements were performed at a pressure of $1 \cdot 10^{-6}$ Pa. The pass energy of the hemisphere analyzer was maintained at 187.85 eV for survey scan and 29.35 eV for high-resolution scan while the takeoff angle was fixed at 45°. Since the samples are insulators, we used an additional electron gun and an $Argon^{+}$ ion gun for surface neutralization during the measurements.

Binding energies of XPS spectra were corrected by referencing the C_{1s} signal of adventitious hydrocarbon to 285 eV. XPS data fittings were carried out with PHI multipak™ software using the Gauss-Lorenz model and Shirley background.

RESULTS AND DISCUSSION

Polymerization yields

Gel content determinations on several cotton fabrics treated with various processes are reported in Table I. Repellan EPF shows the highest values after UV-curing and about similar in thermal one, while Repellan NFC shows lower, although acceptable, yields in UV-curing than in thermal one. In any case, the yields seem independent on UV-curing time and resin add-on. Instead, Oleophobol CP-C gives lower yields either in thermal or UV-curing with a marked dependence on add-on and UV-curing time, hence 60 s are needed to obtain a good yield for a 3% add-on. Plasma polymerization process yields the highest values with Repellan EPF and satisfactory with Oleophobol CP-C but only at 3% add-on.

Water contact angles and wash fastness

Water contact angles measured on treated fabrics are reported in Table II. These have to be compared with 0° measured on untreated cotton, due to immediate adsorption of the drop, so it evidences the high water-repellency conferred by the finish. Measurements on ten different points of the same sample surface were averaged and are in good agreement (standard deviation about 2°) indicating a good homogeneity of the coating. The results obtained with the three types of curing are very close and poorly dependent on add-on and UV-curing time, hence low polymer add-on is enough to modify the fiber surface. Repellan finishes show slightly higher contact angles than Oleophobol, but this yields values practically unaffected by repeated washings, unlike Repellan which generally show a small decrease.

The results confirmed the satisfactory wash fastness of water-repellency finish without differences between thermal, UV or plasma treatment.

Table I. Gel content of fabrics finished with various processes

Resin	Curing type	Add-on (%)	Curing time (s)	Gel content (%)
Repellan EPF	thermal	3	180 (140°C)	92.8
	thermal	5	180 (140°C)	95.7
	UV	3	40	95.2
	UV	3	50	93.9
	UV	3	60	92.7
	UV	5	40	93.6
	UV	5	50	93.7
	UV	5	60	92.7
	plasma	3	30	98.0
	plasma	5	30	99.3
Repellan NFC	thermal	3	150 (150°C)	98.0
	thermal	5	150 (150°C)	97.7
	UV	3	40	79.5
	UV	3	50	79.6
	UV	3	60	81.0
	UV	5	40	80.8
	UV	5	50	82.7
	UV	5	60	80.6
Oleophobol CP-C	thermal	3	180 (140°C)	89.5
	thermal	4	180 (140°C)	69.7
	UV	4	40	67.1
	UV	4	50	78.6
	UV	3	60	90.8
	UV	5	40	41.1
	UV	5	50	52.4
	UV	5	60	67.8
	plasma	3	30	87.1
	plasma	5	30	53.1

Table II. Contact angles of treated fabrics before and after washings

Resin	Curing type	Add-on (%)	Curing time (s)	Contact angle (°)	
				before	after
Repellan EPF	thermal	3	180	140	132
	thermal	5	180	141	135
	UV	3	40	141	132
	UV	3	50	140	133
	UV	3	60	140	133
	UV	5	40	141	133
	UV	5	50	139	133
	UV	5	60	138	136
	plasma	3	30	130	-
	plasma	5	30	138	-
Repellan NFC	thermal	3	150	141	139
	thermal	5	150	139	138
	UV	3	40	140	134
	UV	3	50	138	135
	UV	3	60	139	136
	UV	5	40	142	137
	UV	5	50	141	138
	UV	5	60	140	139
Oleophobol CP-C	thermal	3	180	127	127
	thermal	4	180	130	133
	UV	4	40	126	133
	UV	4	50	126	128
	UV	3	60	131	130

UV	5	40	130	132
UV	5	50	134	129
UV	5	60	129	129
plasma	3	30	132	129
plasma	5	30	127	127

Water vapor permeability

The breathability of a fabric has great importance for comfort. Infact a finish treatment should not cause a loss of its original water vapor permeability. The results reported in Fig. 1 are expressed as WVTR (%) with respect to the original cotton. It is evident that the WVTR is only slightly affected by the finish type without significant differences between thermal, UV or plasma treatment.

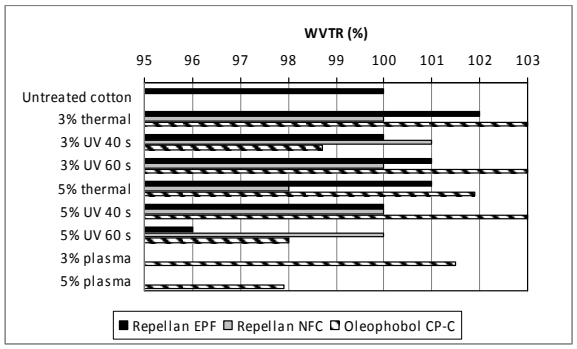

FIGURE 1. Comparison of WVTR determined on finished fabrics

DSC, FTIR-ATR and XPS analyses

In Fig. 2 the DSC traces of fabrics finished with Repellan EPF are compared with that of untreated cotton. The thermal behaviour of cotton results affected by the coating type and dependent on the polymer add-on. Similar results were obtained with the other resins.

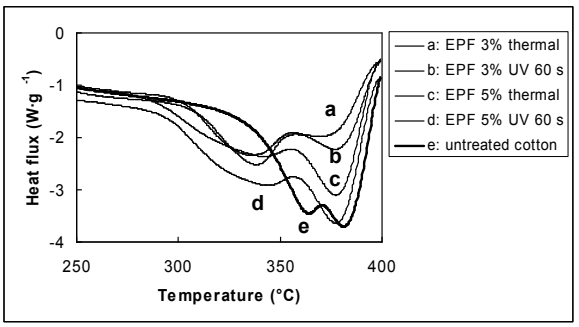

FIGURE 2. Comparison of DSC traces of fabrics finished with Repellan EPF

All the FTIR-ATR spectra of treated cotton showed a sharp peak at about 1740 cm^{-1} assigned to ester moieties in polyacrylate. The absorbance of this peak depends on polymer add-on while appears poorly affected by resin and curing type. Typical peaks due to C-F at 1150 and 1210 cm^{-1} are evident although little overlapped to cellulose peaks.

XPS analysis give the chemical composition of the fabric surface and provides useful information about the fiber coating. Table III shows the relative peak intensities of C_{1s}, O_{1s}, F_{1s} and Cl_{2p} of untreated and finished fabrics.

Table III. Relative intensities in XPS spectra of untreated and resin treated cotton fabrics (3% polymer add-on, 60 s UV curing time)

Resin	Curing type	C_{1s} (%)	O_{1s} (%)	F_{1s} (%)	Cl_{2p} (%)
Untreated cotton	-	60.6	39.4	-	-
Repellan EPF	thermal	42.0	6.1	51.8	-
	UV	43.1	5.7	51.1	-
Repellan NFC	thermal	44.7	10.7	43.3	1.3
	UV	46.0	8.7	43.5	1.7
Oleophobol CP-C	thermal	46.4	7.7	44.7	1.3
	UV	48.0	9.2	41.9	0.9
	plasma	48.6	17.0	33.6	0.8

F_{1s} intensity is about the same for samples thermally or UV-cured, while it decreases in plasma polymerization because O_{1s} intensity increases. Repellan EPF shows the highest fluorine values.

CONCLUSION

UV-curing or plasma polymerization of perfluoro-alkyl-polyacrylates applied as water emulsion on cotton yield water-repellent fabrics as thermal process. The polymerization yields are of the same order of these resulted from thermal curing and high contact angles of water even at lower add-on are obtained. Water-repellency is adequately maintained after repeated washings. Water vapor transmission rates show that the finish treatment, thermal or by UV-curing or by plasma, does not reduce the breathability of the original cotton.

In conclusion, UV-curing and plasma polymerization can be indicated as valid alternative environment-friendly methods to confer water-resistant hydro-repellency to cotton fabrics.

REFERENCES

[1] De, P. et al., UV-resist, Water-repellent Breathable Fabric as Protective Textiles, *J. Ind. Text.*, 34 (2005) 209-222.

[2] Ferrero, F. et al., Water-Repellent Finishing of Cotton Fabrics by Ultraviolet Curing, *J. Appl. Polym. Sci.*, 107 (2008) 810-818.

[3] Periolatto, M., Ferrero, F., Udrescu, C., Finishing of Textile Fabrics by Ultraviolet Curing, *Proceedings of the 9th World Textile Conference AUTEX 2009, Izmir, Turkey, May 26-28, 2009*, pp 355-361.

[4] Mossotti, R. et al., The effect of HMDSO plasma polymerization on the surface and technological properties of wool knitted fabrics, *Vacuum International,* 2 (2008) 68-71.

[5] Guimond, S. et al., Plasma functionalization of textiles: Specifics and possibilities, *Pure Appl. Chem.*, 82 (2010) 1239-1245.

[6] Hegemann, D., Hossain, M.M., Balazs, D.J., Nanostructured plasma coatings to obtain multifunctional textile surfaces, *Progr. Org. Coat.* 58 (2007) 237–240