Superhydrophobic and Oleophobic UV-Curable Surface Engineering of Cellulose-Based Substrates

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ABSTRACT: Cellulose-based materials are one of the most widely used materials provided by nature to mankind. In particular, cotton fibers have been used for millennia to produce clothing items. This wide usage stems from the inherent properties of cotton fabrics such as hydrophilicity and permeability to water vapor. However, increasingly sophisticated uses for cotton-based clothing (e.g., technical textiles) demand specific properties such as hydrophobicity and oleophobicity for repellent functions. The current surface treatments used to attain these functionalities are based on thermally initiated polymerization reactions, using water-based formulations. Thus, the current technologies are energy- and water-intensive. The advantages of using alternative polymerization routes based on actinic radiation are thus clear and include lower energy consumptions, increased processing speeds and smaller plant space. However, example current drawbacks include issues related to the loss of substrate flexibility, breathability and hand. In order to overcome these issues, a durable surface treatment has been developed based on UV-curable polymeric materials that provide superhydrophobic and oleophobic properties to cotton substrates, maintaining intrinsic useful properties of cotton fabrics such as pleasant hand. In this article are reported the innovative surface treatment formulations and procedures developed.

KEYWORDS: Cotton, oleophobic, superhydrophobic, surface treatments, UV curing

1 INTRODUCTION

Currently used surface treatments aimed at providing water and oil repellent properties to cotton substrates are based on polymerization processes initiated by heat, involving the use of solvent or water-based formulations. Thus, the existing technology is very intensive from the viewpoints of chemicals and energy usage. Consequently, an urgent need exists to move to more energy and material efficient processes. A suitable alternative is the use of polymerization mechanisms based on actinic radiation. However, issues such as lack of control over crosslinking and grafting phenomena, leading to loss of properties such as flexibility and permeability, have hindered the evolution of such processes to an industrial scale. Further possible drawbacks of using UV-curable materials include insufficient grafting of repellent species to the cellulosic fibers, which results in decreased wash resistance of the surface treated articles. Therefore,

new surface treatments are required that allow overcoming the aforementioned issues. In this article are reported the latest developments in surface treatments based on actinic radiation, which allow for effective and efficient modification of cellulose-based substrates towards superhydrophobicity and oleophobicity.

Cotton is one of the most widely used materials due to its availability and intrinsic, useful properties. A clear example of such uses is that of sport clothing. In this case it is expected that the inside of the article absorbs sweat and that the outside surface repels rain and stains. This is not possible when using cotton due to its inherent hydrophilicity. Common surface treatments employed by industry include the use of water/solvent-based formulations incorporating hydrophobic materials such as paraffins, siloxanes and fluoropolymers. The most efficient have been demonstrated to be fluor-containing materials, which typically allow for reduction of surface free energy down to 30 mN/m (sufficient to repel oily substances). In order to improve the retention of the repellent functionality, crosslinkers, e.g., based on polyisocyanates, are used to promote grafting of the repellent species to the cellulosic fibers. These surface treatments are

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based on thermally induced polymerization mechanisms. Moreover, the reaction medium is usually water, solvent or combinations thereof. Thus, the energy involved in typical drying and curing stages is very significant.

In fact, the vast majority of current textile finishing processes require significant amounts of chemicals, energy and water. They involve using an aqueous solution or bath to apply chemicals to a textile substrate, fixing the chemicals to the fiber, scouring or washing to remove loose chemicals and drying to produce a finished fabric or garment. Therefore, in these wet processes the amount of water used is very significant, the release of dangerous chemicals to the environment is significant, and they are very energy-intensive due to the heating and later evaporating water operations. In face of the above, it can be expected that, in the interests of energy conservation and cost saving, electron beam, and/or UV-curing techniques will be introduced in textile finishing industrial operations. It has been demonstrated [1] that, in typical (heat-induced) textile processes, the energy involved is an average 210 kJ/m^2, whereas for UV-curing processes it may be as low as 91 kJ/m^2. Also, cellulosic fiber degradation due to excessive heat is avoided when compared to traditional thermal curing processes.

The basic principle is that of using e-beam or actinic radiation instead of heat in order to trigger crosslinking and grafting reactions. Radiation-cured coatings have therefore several advantages: fast curing speeds, high solid content (usually 100% solids), compact curing lines and decreased floor space, ability to cure heat-sensitive substrates, reduced pollution, and lower energy consumption [1–4]. These advantages have led to the rapid growth of the technique in different fields, mainly in the production of colored films and coatings on a variety of substrates, including paper, wood and metal.

In ultraviolet radiation curing, free radicals are generated and the macroradicals couple together to produce a three-dimensional network. A typical UV-curing formulation consists of a monomer and/ or an oligomer bearing multifunctional unsaturated groups, and a photoinitiator that must effectively absorb incident UV light and produce initiating species with high efficiency. The formulation may be 100% solids, meaning that it is 100% reactive (no water or solvents present). Multifunctional acrylates are the most widely used systems. The oligomer is usually a urethane or epoxy chain end capped on both sides by acrylate groups. The molecular weight ranges from 500–3000 Da. Reactive diluents are added to lower the viscosity of the oligomers and to increase the cure rate. The reactive diluents are generally mono- or multifunctional acrylate compounds with a molecular

weight less than 500. In terms of equipment, different types of UV-curing technologies are known, namely medium pressure mercury vapor lamps, electroless vapor lamps, and pulsed xenon lamps.

In the last decades, UV/EB radiation coating technology has evolved significantly both from the raw materials and equipment points of view [2, 5, 6]. An impressive variety of monomers, oligomers, additives and photoinitiators are now available commercially. The variety of materials available allows for tailoring coatings in terms of, e.g., reactivity, flexibility, chemical, heat and abrasion resistance. Also the cost of raw materials tends to reach acceptable values. The problems associated with oxygen-induced reaction inhibition are being overcome through the use of, e.g., cationic photopolymerization. However, it should be mentioned that this type of photopolymerization mechanism is inhibited by the presence of humidity and requires longer radiation times than those typical of radical reactions mechanisms [2]. From the equipment point of view, new lamp technologies, including UV LEDs, have been introduced to the market in the last years. However, the myriad of raw materials alternatives and the latest equipment developments have not been explored conveniently in the context of textile surface treatments. These substrates present additional difficulties related with their intrinsic porosity, yarn structure, etc., that have so far hindered the development of consistent solutions. When deposited on a yarn, a droplet of wetting liquid spontaneously wicks into the yarn due to capillary forces associated with the given structure and geometry of the void spaces (interstices) between yarns or filaments. This phenomenon causes limited light penetration into the yarn, which in turn limits the depth of cure [7]. An incomplete degree of curing is unacceptable due to residual odor of acrylate polymers and also to concerns over the toxicity of certain chemical residues (such as photoinitiators and monomers) on fabrics that may be used for garments worn next to the skin. Other example requirements of textile coatings that have not yet been met in industrial applications of UV-curing processes include excellent flexibility (which influences the handle and drape of the fabric), permanent bonding to the textile substrate and chemical/abrasion resistance.

The study of UV curing of textile substrates can be traced to the work of Walsh *et al.* [8, 9], related to the back-coating of nylon-viscose upholstery fabric (usually done by a thin latex coating), and to the pioneer work of Guthrie *et al.* [10] related to grafting of styrene onto cotton. As these references indicate, since its origins the UV-curing application on textiles has been divided into two categories: surface coating and surface grafting/crosslinking.

In the work of Walsh, the UV coating formulation was transfer coated onto the fabric and cured by UV radiation [8]. The flexural rigidity and yarn ravelling tests showed that UV-cured samples were comparable to the latex-coated samples. Studies were also conducted to achieve thicker coatings for synthetic leather applications, by radiation cure process, instead of the conventional solution-based polyurethane coating [11]. Most of the latest reports on application of UV-curable coatings in textiles relate to coloration/digital printing processes [12, 13]. Textile printing studies have been carried out at the TNO laboratory in Holland [7, 12], where Marsman and coworkers performed studies on UV-curable coatings and the development of UV-curable binders for pigment printing. In research work carried out by Fouassier et al. [5], a UV printing paste was developed based on a trifunctional oligomer, a thickener (aqueous solution of synthetic, high polymer, acrylate-based thickening agent in the form of a medium-viscosity, slightly ammoniated paste), an emulsifying agent (copolymer of ethylene oxide and propylene oxide), pigments (red, yellow and blue), and various photoinitiators (considering the absorption ranges of the three pigments in the near UV and visible ranges). A process of dyeing or printing textile fabrics with reactive dyes and then UV curing has been patented by Fritzsche (US Patents 5409504 (1995), 5597388 (1997) and 5679115 (1997)). A cotton satin fabric is printed with a print paste that contains: reactive dye, oligomer, monomer, urea, sodium alginate and, as photoinitiator, a mixture of benzophenone and phenyl-(1-hydroxycyclohexyl) ketone. The prints are dried and then irradiated under two mercury high-pressure lamps (50 W, 436 J/cm^2) on each side of the fabric, at a transport speed of 10–20 m/min. After UV curing, the prints are conventionally washed off (cold and hot).

In the field of textile surface grafting/crosslinking processes, radiation curing has been proposed to modify natural (wool [14, 15], silk [16], linen [17], cotton [18–20] and other cellulose-based materials [10, 21]), and artificial fibers (PP [22], PET [23, 24]) for moisture management/hydrophobicity [19, 20, 23–25], soil release [3], durable press (wrinkle resistance) [18], abrasion resistance [3], shrink resistance, flame retardancy [26], and dyeability [16]. The published studies concern grafting and crosslinking using basically styrene [10, 21], acrylates [23], metahcrylates [18, 20, 22, 23], epoxy [20], acrylamide and their derivatives. In the context of methylolcellulose regeneration and derivatization processes, Guthrie [10] reported the photoinduced grafting of styrene onto cotton cellulose by initial methylolation using the cellulose/DMSO/HCHO system. Continuous photografting/crosslinking of polyethyleneglycol dimethacrylate oligomers onto cotton, using a water-soluble benzophenone photoinitiator, was investigated by Jang et al. [18], aiming at a durable press finish. The photografting increased the wrinkle resistance of cotton with both surface crosslinking and bulk crosslinking occurring via dual curing of a mixed formulation containing both a thermally curable component (1,2,3,4-butanetetracarboxylic acid/sodium hypophosphite) and a UV-curable component. Hon and Chan [21] have studied the use of photoinduced free radicals generated in cellulose and cellulose derivatives, for grafting reactions. Reine and colleagues [25] studied the copolymerization of acrylamide monomers onto cotton using photoinitiated polymerization. Large increases were observed in the moisture regain of the modified cotton, as compared with cotton fabric control samples.

With regard to the achievement of repellent properties in textiles, the most relevant advance reported concerns the development of UV-curable PDMS-containing polyurethane oligomers (not available commercially to the best of our knowledge). Reference can be found to the use of this oligomer type for textile (PET, nylon) surface treatment with a long-lasting hydrophobic property [24]. However, most of the oligomers used have high viscosity, making it difficult to manipulate them and, therefore, they must be diluted with a reactive diluent. But increasing the functionality of the diluent will increase the crosslinking density in the cured film and, therefore, its rigidity. On the other hand, the abrasion resistance of the surface treatment is directly related to the crosslinking degree. The right balance must therefore be found. In another research work, cotton fabrics were functionalized by combination of thermal and radical photopolymerization of perfluoro polyacrylates [19, 20]. After impregnation with a water emulsion of a commercial agent each textile sample was firstly thermal- (2–3 minutes at 140–150 °C) and then UV-cured with a medium-pressure mercury lamp under nitrogen atmosphere. Contact angle, moisture adsorption, and vapor permeability measurements were performed. The authors concluded that the finish treatment by thermal as well as UV curing does not reduce the breathability of cotton fabric. It should be mentioned however that the impregnation method used involves the use of large amounts of formulation and the generation of significant waste material. In a recent publication, Miao et al. [27] have reported the use of γ-ray-induced grafting of perfluoroalkyl phosphate acrylate for imparting high water and oil repellence to cotton. The contact angles for water and sunflower oil were determined to be over 150° and 140°, respectively. Mention should be made of the fact that the high costs associated with the use of γ-ray sources in industrial environments, such as those of

textile finishing industries, makes this process not amenable to industrial implementation.

In this paper is described a cotton grafting/crosslinking process, based on actinic radiation (such as that produced by widely available industrial equipment) and using commercially available photoreactive compounds which include perfluorocarbon chains, thus leading to superhydrophobic and oleophobic properties. The process developed involves the use of ultrasonic (US) spraying and therefore the viscosity of the formulations had to be carefully maintained at values relatively close to that of water. When compared to existing UV radiation-based processes described in the literature, our methodology has the following advantages: wide availability of commercial equipment and raw materials, use of minimal amounts of formulation, no waste material and ability to treat only one side of the substrate (due to the use of US spraying, under specific conditions), excellent hand, flexibility and wash fastness of treated substrates. These characteristics add to the abovementioned advantages of using a UV radiation curing process (lower energy and material consumption, smaller plant space, shorter processing times, etc.) instead of thermally induced polymerization reactions. The polyisocyanate and perfluoropolyether-urethane dimethacrylate used are commercially available and widely used in surface coatings market applications. Therefore, their usage sustainability is not expected to be an issue. The described technology has been patented (PT 105534 (2012): "Functionalisation of cellulosic substrates for superhydrophobic and oleophobic properties by using actinic radiation curing formulations").

2 EXPERIMENTAL PROCEDURE

2.1 Materials

The cotton substrate was a mercerized cloth pretreated with a flame system in order to remove any waxes used during its production. The presence of these processing aids could otherwise influence the repellency properties of the textile substrate. Mercerization converts the structure of the fiber from alpha-cellulose to a beta-cellulose polymorph (more favorable thermodynamically). As a consequence of the swelling of the cell wall the cotton fiber surface area increases, which facilitates finishing operations.

Dipropylene glycol diacrylate (reactive diluent, SR508 from Sartomer, used as received) and a perfluoropolyether-urethane dimethacrylate were used as monomers. The photoinitiator used was 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173, available from Ciba Specialty Chemicals). As co-solvent, 1-propanol (Sigma-Aldrich) was used as received. A polyisocyanate (Basonat® from BASF) was used as crosslinking agent.

2.2 Equipment

The ultrasonic spraying deposition system used was a Lechler atomizer type US2, complemented with a peristaltic pump.

For UV curing, a R2000 radiometer (OmniCure Series 2000 System) unit was used. It is equipped with a 200 W mercury short arc lamp and allows for a maximum irradiance level of 30 W/cm². The lamp spectrum is characterized by peaks at 360, 400 and 440 nm.

2.3 Methods

The formulations were prepared by mixing the reagents in the following order (under constant agitation): 1-propanol, Darocur 1173, SR508, perfluorocarbon dimethacrylate and polyisocyanate. The US deposition in cotton substrates (10 × 10 cm) was carried out using a flow rate of 5 mL/min, an ultrasonic power of 50% (relative scale), a supply of compressed air at 0.25 bar, and a deposition time of 30 s. The 1-propanol was then removed by gentle drying at 100 °C for 2–3 min in a laboratory stove. UV curing was typically performed under a nitrogen feed and at an irradiance level of 25 W/cm². In order to ensure full cure, the samples were irradiated for 5 min. For assessing the wash fastness the following procedure was adopted: a) the treated samples was pre-washed with ethanol in order to remove residual monomer that could polymerize during the following washing operation; b) the pre-washed samples was then washed in a solution of standard detergent (2 g/L, SDC reference detergent type 3) at 90 °C, under vigorous agitation, for 2 h (1 g of sample per 20 mL of washing solution); c) the washed sample was dried at 80 °C for 40 min in order to assure thorough drying at a relatively low temperature.

2.4 Characterization

In the context of preliminary studies, a rapid assessment of hydrophobicity and oleophobicity was carried out by measuring the average time (min) five standard droplets (0.02 mL) of either distilled water or mineral oil (GALP HIDROLEP 46) took to be absorbed by the treated substrates. This was quantified as water repellency time (WRT) and oil repellency time (ORT).

In following experiments, the hydrophobicity and oleophobicity were evaluated by determining the static contact angle (sessile drop method, t = 2s) formed between the repellent surface and a droplet (3 µL) of water and oil, respectively. To this end, an

OCA 20 (DataPhysics Instruments) contact angle system, was used. The reported values correspond to the average of 10 measurements.

The surface chemistry was analyzed by means of a FTIR-ATR unit (PerkinElmer 100). The following parameters were used: resolution 4 cm^{-1}, 10 scans, wave-number scan from 650 to 4000 cm^{-1}.

Optical microscopy (Leica DM2500 M) was used to evaluate surface morphology changes due to the treatment.

Table 1 Composition and properties of the treatment formulations.

Component/Formulation (% w/w)	F1	F2	F3	F4	F5
SR508	0	0	70	69	79
Polyisocyanate	0	5	5	5	5
Darocur 1173	5	5	5	5	5
1-propanol	94	89	20	20	10
Perfluorocarbon dimethacrylate	1	1	0	1	1
Viscosity (cP)	8	8	10	10	15
Solid contents (% w/w)	6	11	80	80	90

The formulations viscosity is a critical factor in the developed procedure as the maximum value that allows for an efficient use of the ultrasonic atomizer is ca. 20 cP. The unit used for viscosity measurement was a Fungilab Smart L equipped with a LCP Low Viscosity Adapter (30 rpm, room temperature). The typical viscosity of the formulations studied was in the range of 10–20 cP.

3 RESULTS AND DISCUSSION

Initial formulations were designed in order to evaluate the effects of dipropylene glycol diacrylate, perfluoropolyether-urethane dimethacrylate and polyisocyanate on cotton's repellency. For this purpose formulations F1 to F5 (see Table 1) were prepared and used for the treatment and characterization of cotton samples as described in the Experimental Section. The water repellency time (WRT) and the oil repellency time (ORT) were determined for the treated surfaces (facing the spraying unit – face), respective back sides, before and after the washing procedure.

In Figure 1, the WRT and ORT values for the face of these samples, prior to the washing procedure are presented. From the analysis of Figure 1, it can be observed that the combination of the
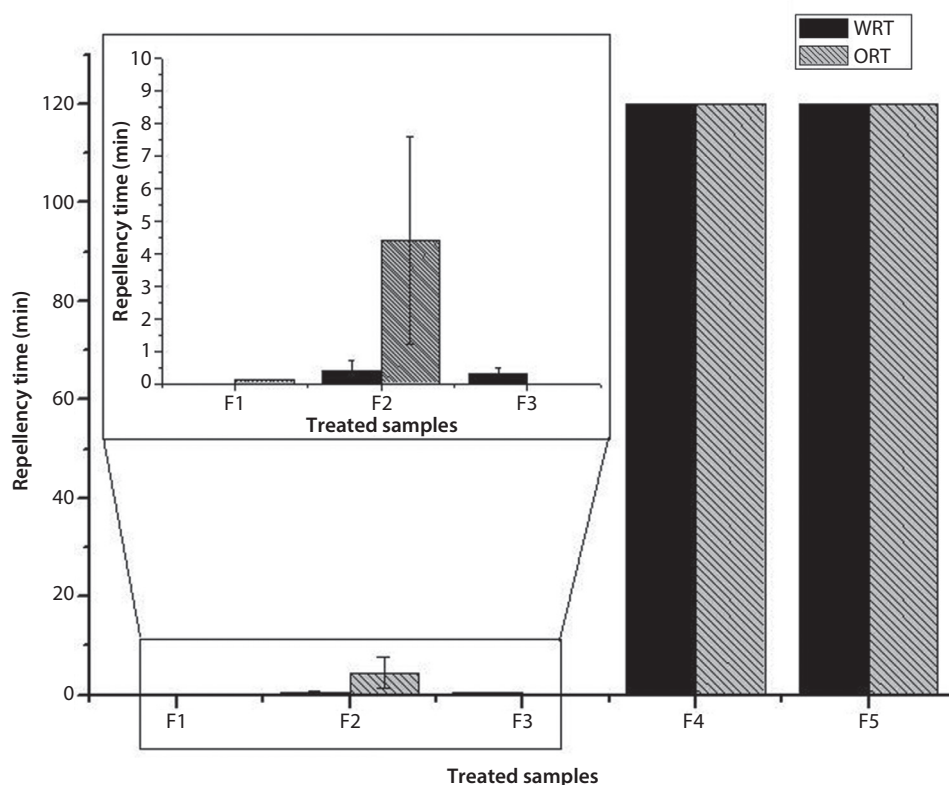

Figure 1 Water and oil repellency times (face) for samples treated with formulations F1 to F5 (unwashed).

perfluoropolyether-urethane dimethacrylate and the photoinitiator (formulation F1) does not allow for the achievement of repellent properties. The high proportion of 1-propanol, and low proportion of the perfluorocarbon, probably causes the complete absorption of the perfluorocarbon into the bulk cotton, which results in lack of repellency of the treated surface. When the polyisocyanate is added (formulation F2), a small increase in both the water and oil repellency is observed, due to thermal curing that occurs in the 1-propanol removal stage (100 °C, 2–3 min.) The relatively high standard deviation associated with ORT is related to heterogeneity of the treated surface (from the chemical point of view). The observed WRT and ORT values are interpreted as a consequence of crosslinking/grafting reactions occurring between the hydroxyl groups in the cotton fibers and the isocyanate groups of the crosslinker, originating urethane functional groups. The crosslinking of the cellulosic fibers and the decrease of the available hydroxyl groups lead to an increase of the hydro- and oleophobicity of the treated substrates. Mention should be made of the fact that although crosslinking has occurred, the flexibility and hand of the cotton samples have not been affected. When the perfluorocarbon is absent from the formulation, and the dipropylene glycol diacrylate is added at a 70% loading (formulation F3), a low water repellency and a lack of oleophobicity are observed. The hydrophobicity is thought to originate mainly from the crosslinking reactions between the hydroxyl and isocyanate groups, present in the cellulosic fibers and crosslinker, respectively. The lack of oil repellency derives from the absence of the perfluorocarbon. This observation is supported by the fact that samples treated with F1 and F2 do present some oleophobicity. In the case of the sample treated with F2 the oleophobicity is greater, probably due to a greater surface concentration of perfluorocarbon macromolecules. It is expected that the crosslinker will migrate less than SR508 or the perfluorocarbon, due to its greater viscosity and possible formulation component segregation during atomization. In the sample treated with F2 this results in a greater repellency of the treated surface. This is not the case in the sample treated with F3 due to the fact that SR508 does not have a low enough surface tension (namely when compared to that of the perfluorocarbon).

The back of samples treated with formulations F1 to F3 did not show water or oil repellency, before and after washing. Thus, it can be concluded that the treating formulation components responsible for the repellency effect, namely the polyisocyanate and the perfluorocarbon, did not migrate efficiently to the back.

With regard to the samples prepared with formulations F4 and F5, the WRT and ORT measured values

(before and after washing, face and back) were greater than two hours. Therefore, it was concluded that the combined use of SR508 and the perfluorocarbon results in excellent water and oil repellency properties. This is interpreted in light of the excellent miscibility between SR508 and the perfluorocarbon used. Along with the presence of 1-propanol, this causes a homogeneous distribution of the perfluorocarbon through the cotton substrate and efficient grafting and crosslinking reactions that result in the incorporation of the perfluorocarbon in the polymeric matrix formed upon photopolymerization.

In following studies, the amount of grafted/reticulated polymer, and the grafting/crosslinking efficiency, in samples prepared with formulations F4 and F5 (see Table 2) were determined by gravimetric analysis. The water and oil repellency of samples treated with formulations F4 and F5 were characterized by measuring the values of contact angles with water and oil, respectively (Figures 2 and 3). The face (facing the ultrasonic atomizer) and the back were studied. The surface chemical composition of several samples was assessed by FTIR-ATR (Figures 4 and 5) in an attempt to confirm the surface modification. Finally, images

Table 2 Polymer grafting/crosslinking weight and efficiency.

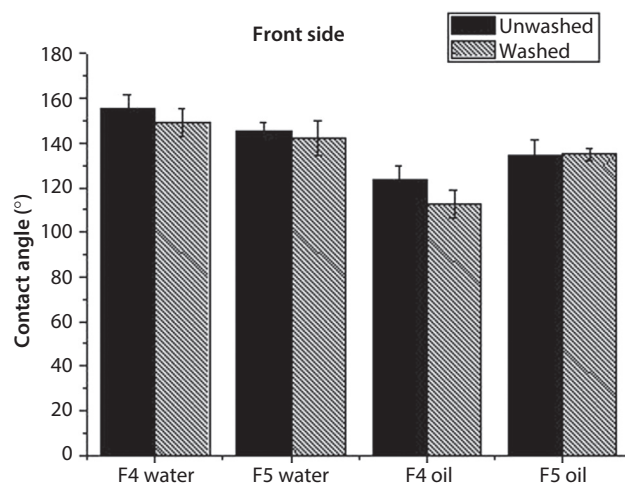| Weight (g/m²)/Formulation	F4	F5
Untreated cotton	200.0	
After formulation deposition	226.0	238.0
Before washing	221.1	234.2
After washing	218.6	236.2
Grafted/Crosslinked polymer (% w/w)	8.5	15.3

Figure 2 Water and oil contact angles for samples treated with formulations F4 and F5: face side.
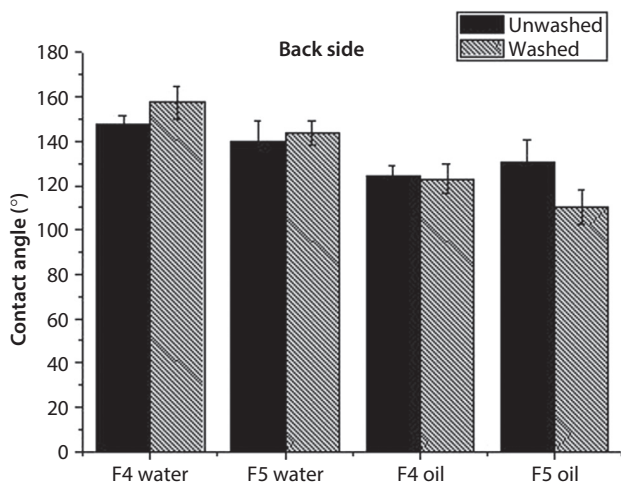
Figure 3 Water and oil contact angles for samples treated with formulations F4 and F5: back side.
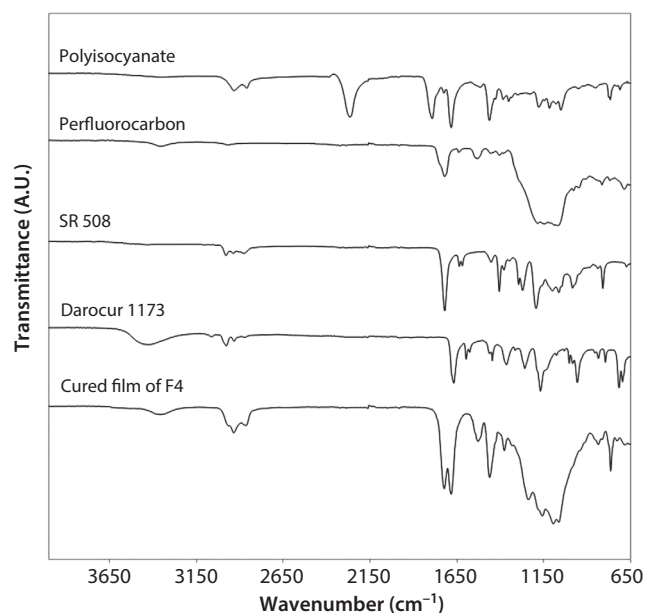

Figure 4 FTIR-ATR spectra for the formulation components and cured film of F4.

Figure 5 FTIR-ATR spectra for samples of cotton treated with formulation F4.

Figure 6 Images of unwashed (**a**) and washed (**b**) samples of cotton treated with formulation F4.

Figure 7 Optical microscopy images of face (**a**) and back (**b**) samples of untreated cotton.

obtained from the contact angle equipment (Figure 6) and by optical microscopy (Figures 7, 8 and 9) were obtained so as to analyze changes in surface morphology due to the surface treatment.

In Table 2 are presented the weight: a) of the treated substrate after the formulation deposition and before the drying and photopolymerization steps, b) after these steps but before washing, and c) after washing of cured samples. The typical standard deviation of the measurements was ± 2.0 g/m².

In Figure 2 it can be observed that both formulations F4 and F5 result in superhydrophobic surfaces (face side), with contact angle averaging 150°. Upon
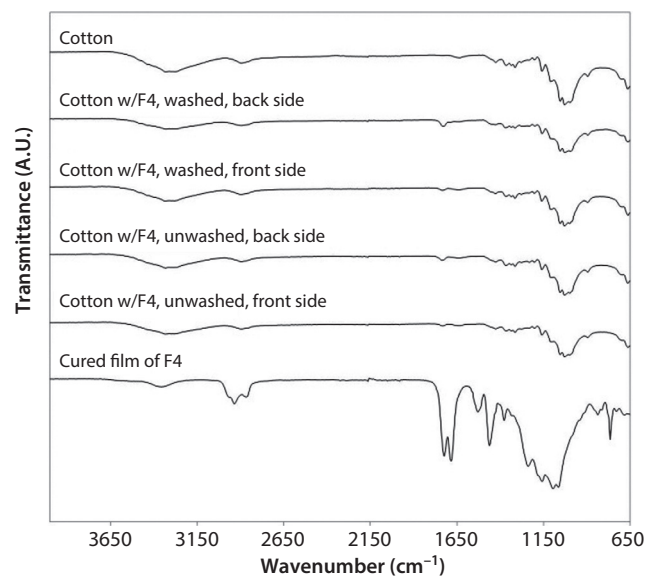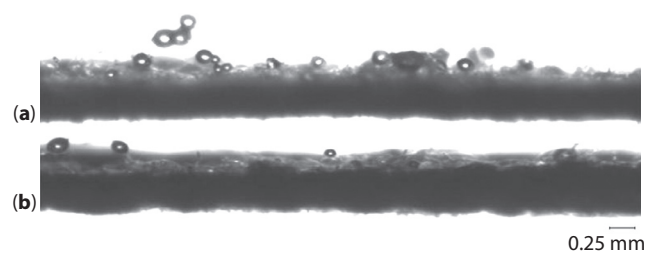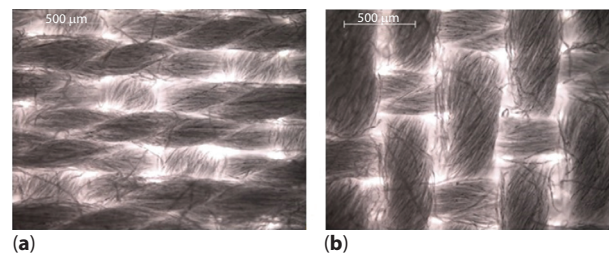
intensive washing, this property is retained, which indicates extensive grafting and crosslinking of the perfluorocarbon and SR508. The water repellency of samples treated with F4 is slightly greater than that of samples treated with F5. However, bearing in mind the standard deviation of the average values, namely for the washed samples, this effect can be considered as not being significant. In terms of oil repellency, it is observed that the sample treated with F5 has higher contact angles with oil and that this excellent
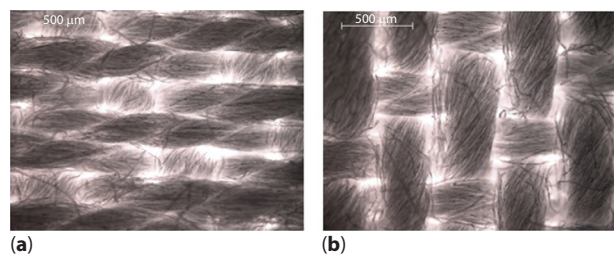
Figure 8 Optical microscopy images of unwashed (**a**) and washed (**b**) samples of cotton treated with formulation F4: face side.
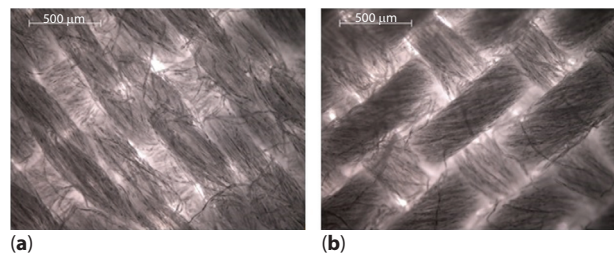

Figure 9 Optical microscopy images of unwashed (**a**) and washed (**b**) samples of cotton treated with formulation F4: back side.

repellency (close to superoleophobicity) remains after extensive washing. The lower oil repellency of samples prepared with F4 is thought to be due to the greater proportion of 1-propanol and lower proportion of SR508, which leads to more pronounced migration of the perfluorocarbon macromolecules through the bulk of the cotton substrate.

This interpretation is supported by the results presented in Figure 3, namely relating to the washed samples. Here, it can be seen that the oleophobicity of the back of washed samples is greater for substrates treated with F4 than with F5. In the case of the latter, it can also be observed in Figure 3 that the washing procedure leads to a significant decrease of oleophobicity, which is attributed to release of unbound perfluorocarbon macromolecules. As far as the hydrophobicity of the back is concerned, it can be observed in Figure 3 that, although similar values are obtained before washing, the water repellency for samples treated with F4 is greater than that of samples treated with F5. This effect further supports the evidence that a greater amount of 1-propanol, and lower amount of SR508, leads to increased migration of the fluorocarbon macromolecules through the bulk of the cotton substrate. It can also be observed that, generally, the wash resistance is significant and that the back of the samples treated with F4 has more unbound SR508 that is removed upon washing, leading to an increased exposure of the perfluorocarbon chains and increased contact angle with water.

In Figure 4 are presented the FTIR-ATR spectra of the components of formulation F4 and that of a film of this formulation cured according to the conditions described previously.

From the observation of Figure 4, it can be concluded that the isocyanate group peak at 2285 cm^{-1} is absent from the cured film. This indicates a complete, thermally induced conversion of the polyisocyanate to urethane groups through reaction with the cotton hydroxyl groups, a fact that contributes to the reduction of the cotton hydrophilicity.

In Figure 5 are presented the FTIR-ATR spectra of control (untreated) cotton samples of a cured film of F4, and of the unwashed, washed, back and face of a cotton sample treated with this formulation.

The spectra of the cotton samples are very similar, a fact that is thought to be due to the typical 3 μm depth analysis attainable with FTIR-ATR. The changes in repellency observable in the contact angle measurements are therefore a consequence of surface and bulk chemical modification of the cellulosic fibers by crosslinking and grafting of the polyisocyanate and acrylates present in the treatment formulation. Nevertheless, in Figure 5 it can be noticed that the isocyanate group peak at 2285 cm^{-1} is absent from the control and treated cotton samples and that the acrylate group peak at 1750 cm^{-1} is more pronounced in the back side of the treated samples. This latter evidence indicates that in the back side there is a higher concentration of unreacted acrylate groups, which is in agreement with the fact that the UV light is applied in the face, and with the reported difficulties in obtaining a through cure profile in porous substrates due to the existence of "shadow" areas were the UV radiation level is low. Nevertheless, bearing in mind the results obtained after the intensive washing procedure, it can be concluded that the polymeric matrix, formed on exposure of the treated cotton substrate to UV light, is strongly attached to the cellulosic fibers.

Images of a sample of cotton treated with formulation F4 were obtained by using the camera included in the contact angle measurement unit. In Figure 6 it can be seen that the surface of the sample side facing the ultrasonic atomizer (and the photocuring equipment) presents spherical particles. These correspond to cured droplets of the treatment formulation. Therefore it is expected that their main composition is cured SR508. It can also be seen that upon washing, the surface concentration of cured droplets is significantly reduced. Therefore, the cured droplets correspond to the formulation that was not absorbed by the cotton and that is not bound to the cellulosic fibers (after UV curing).

In Figure 7 are presented images obtained by optical microscopy, corresponding to the face and back of a sample of untreated cotton. In Figures 8 and 9 are

presented images obtained by optical microscopy, corresponding to the face and back, respectively, of a sample of cotton treated with F4, before (a) and after (b) the washing procedure.

The observation of the images in Figure 8 confirms the analysis of the images in Figure 6. Part of the atomized formulation was not absorbed by the cotton and originated cured droplets that in general are removed upon washing. It should however be mentioned that the hand and flexibility of the treated samples after washing are acceptable and close to those of the untreated cotton. It should also be noted that, besides the presence of discrete spherical particles, no coating layers can be seen covering the fibers and spaces in between. The images seen in Figure 7 (control sample) and 9 (back of treated samples) do not show any differences in morphology. Therefore, it is concluded that the surface modification has been achieved successfully, without visible coating layers that could otherwise affect the hand, flexibility and permeability of the treated cotton.

4 CONCLUSIONS

From the above presentation and discussion of results it can be concluded that:

1. SR508 and the perfluorocarbon used are very miscible and when used in combination, along with the polyisocyanate, allow for a homogeneous and efficient fixation of the perfluorocarbon to the polymeric matrix formed upon photopolymerization;

2. At the back side of the treated substrate the concentration of unreacted acrylate groups is greater than that of the face side, due to the existence of "shadow" areas that cause differences in the UV radiation level available through the bulk cotton;

3. The surface treatment composition and procedures represented by formulations F4 and F5 result in the attainment of superhydrophobic ($\approx 150°$) and highly oleophobic (120–130°) cotton, with excellent wash fastness;

4. The repellency values of the face and back surfaces can be tailored by adjusting the amount of 1-propanol and SR508 in the treatment formulation;

5. The hand and flexibility of the modified cotton are not affected by the surface treatment, i.e., no fiber or pore coating occurs at the macroscale, due to the ultrasonic atomizing deposition process used and to the low viscosity of the formulation developed.

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