UV Treatments on Cotton Fibers

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UV Treatments on Cotton Fibers

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Abstract

Ultraviolet (UV) radiations can act in different ways on the functionalization of textiles, through pre- or posttreatments, in order to modify their behavior in dyeing and finishing processes. In cotton fiber, unlike the wool, the UV absorption is not due to any of the structural groups of the normal cellulosic chains and can only be attributed to “impurities” or “faults” bearing carbonyl and/or carboxyl groups. In fact, UV irradiation coupled with mild oxidation can improve some properties of the cotton fibers such as pilling resistance, water swelling, and dyeability. Therefore, the process of differential dyeing with direct and reactive dyes assisted by UV irradiation was studied and interesting differential chromatic effects were obtained by a UV posttreatment capable to fade dyeing. On the other hand, the surface modification of cotton fabrics by UV curing and UV grafting with suitable chemicals was pursued to obtain finishing treatments able to confer oil and/or water repellency. Finally, antimicrobial finishing by chitosan UV grafting was proposed as valid environmental friendly method to confer a satisfactory washing-resistant antimicrobial activity to cotton fabrics even with low polymer add-on.

Keywords: cotton, dyeing, finishing, UV curing, UV grafting, UV radiation

1. Introduction

Cotton fiber differs markedly from other cellulose fibers in morphological traits. Due to its many features, cotton, even though it was discovered later than other fibers, gained a high position and strongly stimulated the development of textile industry. Cotton today is the most used textile fiber in the world. Its current market share is 56% for all fibers used for apparel and home furnishings; another contribution is attributed to nonwoven textiles and personal care items. It is generally recognized that most consumers prefer cotton fiber for personal care items to those containing synthetic fibers.

Soft hand, good absorbency, and color retaining are among the advantages of cotton fabric; it is easy to print, handle, and sew; it is machine-washable and dry-cleanable; and it has good strength and hangs well. These are all the desirable properties for a textile but, for some applications, they can show drawbacks, which suggested modifications of the fibers achievable with chemical or physical treatments. Among the latter, ultraviolet (UV) irradiation was experimented.

UV radiations can act in different ways on the functionalization of textiles, through pre- or post-treatments, in order to modify their behavior in dyeing and finishing processes.

The UV treatments applied in textile field, in addition to required specific effects, should also have the following advantages: (1) easy application, not needing expensive and sophisticated equipment; (2) durability and fastness of the degree of treatment looking at the future uses; (3) limited treatment costs, without precluding any market segment; and (4) environmentally friendly requirements, for sustainable textile processes. Many research works were developed with the aim to utilize the effects of UV radiations on various natural as well as synthetic fibers [1–6]. Most of these studies were devoted to the surface modification of wool, but even cotton fiber was considered.

In cotton, unlike the wool, the true origin of the UV absorption, which is not due to any of the structural groups that make up the normal cellulosic chains, is uncertain and can only be attributed to “impurities” or “faults” bearing carbonyl and/or carboxyl groups.

Naturally pigmented green cotton fiber derives its color from caffeic acid that is deposited in alternating layers with cellulose around the outside of the fiber. The isolated compound is fluorescent (287 and 310 nm absorption wavelengths), and it has been theorized that its purpose is to absorb UV radiation in order to protect the seed. Brown and tan cottons derive their color from tannin vacuoles in the lumen of the fiber cells rather than in the wax layer as in green cotton. The brown color appears after the fibers are exposed to oxygen and sunlight, which happens when the seed pod opens.

The gray cotton fiber contains the above-cited impurities, so one or more pretreatment processes before dyeing are applied to attain its full textile exploitation. The pretreatment processes of cotton fabrics include scouring to get off noncellulosic impurities, pigments, and waxes. An oxidative bleaching is carried out to wipe out natural coloring matter for white or dyeing, while singing is applied to eliminate the protruding loose fibers [7].

Mansuri et al. [8] claimed that cotton-knitted fabric padded in a solution of hydrogen peroxide and then irradiated with UV lamp showed a significant pilling reduction, comparable to that obtained with industrial system of biopolishing. Moreover, Millington said that Siroflash® treatment (UV irradiation coupled with mild wet oxidation with hydrogen peroxide) is highly effective against pilling formation of wool as well as of cotton fiber [9]. In the latter case, the application of Siroflash® process would require the presence of a sensitizer or a photoinitiator to absorb UV radiation in the primary photochemical step. Such a photoinitiator must be odorfree, nontoxic, low expensive, and easily removable by aqueous washing. This rules out many of the commercial UV photoinitiators, but hydrogen peroxide is able to absorb UV radiations below 300 nm to produce highly reactive hydroxyl radicals. One would expect these radicals to reduce the strength of knitted cotton fabric by breaking the cellulose chains. In fact, significant dry-burst strength losses were observed in dependence on hydrogen peroxide concentration, but some fabric strength loss would be acceptable if the limiting factor is an unacceptable level of pills.

Mercerization is the treatment of cotton yarns, fabrics, and knit goods with cold, strong caustic soda bath under tension to give increased luster, smoothness, dye and finishing chemical uptake, dimensional constancy, and better mechanical properties. Zuber et al. [10] demonstrated that UV rays have a similar effect, on cellulosic fibers, as the alkaline treatment; irradiated cellulosic fibers showed higher swelling in comparison with any concentration of soda treatment, but tear and tensile strength were worse compared to the untreated and to the alkali-treated ones. They emphasized that UV rays do not produce loss in weight after exposure of cotton fabrics, and affinity for direct dyes is slightly enhanced in comparison with that found with mercerization. However, with a reactive dye it is found that UV irradiation not only enhanced the strength of dye on irradiated fabric but also improved the dyeing properties [11]. The reason for this might be that the exposure of cotton fiber to UV radiation in the presence of oxygen causes cellulose oxidation to carboxylic acids and opens spaces between the fibers causing imbibition of more dye, hence the interaction for dyeing becomes more significant [12].

Iqbal et al. [13] and more recently Adeel et al. [14] observed that UV radiation not only enhances the uptake and fastness of natural dyes on pre-irradiated cotton fabric using low concentrations of dye but also with a low concentration of mordant.

Cotton fiber immersed in water develops a negative surface potential, which consequently gives rise to electrostatic repulsion of anionic dyes. Therefore, a large amount of electrolyte, such as sodium sulfate or chloride, is required in order to reduce the repulsion between the negatively charged fibers and the anionic dyes. Moreover, the complete dye exhaustion is not normally reached, causing environmental problems due to the discharge of colored effluent having a high salt concentration. To overcome these problems, the cationization of cotton fiber was applied to increase the substantivity of anionic dyes by introducing positively charged sites on the fibers. Pretreatments with glycidyltrimethylammonium chloride and other cationization reagents were reported. However, cationic polymerizable monomers, such as methacryloyl quaternary ammonium compounds, have also been fixed onto cotton fabric using UV radiation with a view to producing print-patterned dyeings [15].

Instead, Jang et al. [16] have examined the potential of photografting cationic monomers onto crease-resistant cross-linked cotton fabric by incorporation of a water-soluble photoinitiator to improve grafting. In fact, whereas untreated cotton is readily dyeable with anionic dyes in the presence of salt, the cross-linked fiber is undyeable to a comparable deep shade, since the diffusion of relatively large dye molecules into the cross-linked substrate is hindered by a low swelling under aqueous conditions. The dyeability of cationized cotton fiber by three classes of dyes (direct, reactive, and sulfur dyes) has been significantly improved owing to the increased ionic attraction between dyes and cationized cellulose, even in the absence of salts [17].

On the other hand, Dong and Jang [18] proposed the direct photografting of wool-reactive dyes themselves onto cotton fabric. This coloration utilizes the photoreactivity of certain dyes under UV irradiation, through photopolymerization, photografting, and photocross-linking processes, to form a polymerized and cross-linked dye network. Thus, a single class of dye can color almost any textile substrate since no specific affinity of particular dyes to individual fibers is required. Reactive dyes containing an α-bromoacrylamido reactive group are among the most successful metal-free dyes for protein fibers because of their brilliant color and high wet-fastness properties. However, these reactive dyes hardly react with cotton fiber under similar conditions owing to the rather low nucleophilicity of the hydroxyl groups in cellulose compared with the thiol and amino groups in proteins. Therefore, dyes containing α-bromoacrylamido groups were employed as grafting monomers to be photografted onto cellulose under continuous UV irradiation. This novel approach may realize the photoactive coloration of cotton fiber even with dyes of low affinity for conventional reactive dyeing. Furthermore, the coloration does not require large amounts of salt, time, and energy, which makes it an alternative process of excellent environmental friendliness.

2. Differential dyeing on cotton fabric by UV irradiation

2.1. Differential dyeing

Textile world is always looking for new color effects, both for artistic questions and in order to meet the current fashion demands; for these reasons, differential dyeing effects mainly on wool fibers were studied. These can be achieved by surface modification on selected areas of fabric by a physical surface treatment such as plasma [19] or UV irradiation on one side followed by a conventional dyeing [20]. Moreover, patterning effects can be obtained if a suitable mask is interposed between energy source and fabric for selective surface modification. This represents an alternative and less expensive method than the usual production of patterned fabrics by printing or color weaving.

In the Sun-Wash method patented by Nearchimica with Stamperia Emiliana (Italy) [21], the continuous UV pretreatment of wool fabric on one face before dyeing has been proposed to obtain different shades on the two faces or patterning effects. A careful selection of dyes is needed to obtain satisfactory tone-on-tone effects and even more to produce double-face effects with different colors. These suggestions inspired the experiments on differential dyeing of wool by UV irradiation carried out by Migliavacca et al. [22]. A good final shade uniformity was obtained, with an acceptable color difference ($\Delta E \geq 5.0$) between UV-treated and untreated fabric area (double-face effect), due to an increased dye-fiber affinity of the side previously treated with UV radiation.

The same type of chromatic effect was also wanted for cellulosic fibers, in particular for cotton [23]. An unscoured 100% cotton yarn was chosen (N_m = 2/34), and from this material many knitted fabrics were prepared in order to do dyeing tests with direct dyes. At first, these fabrics were subjected to a dynamic UV irradiation under a Hg-medium pressure vapor lamp, with the following parameters:

UVA irradiance:	430 mW/cm^2
source working length:	0.6 m
radiant exposure:	8.6 J/cm^2
fabric speed:	11 m/min
no. of irradiation steps:	6
total irradiation time:	30 s

Colorimetric measurements were made comparing the UV-treated fabric with the untreated one, using a reflectance spectrophotometer Datacolor Check II Plus, with the results reported in **Table 1**.

Sample	Δ*L*	Δ*a*	Δ*b*	Δ*E*
UV treated	−0.65	−0.18	2.86	2.94

Table 1. CIE L a b difference parameters for unscoured cotton fabric after UV treatment.

In these conditions of treatment, a global fiber-yellowing effect is observed, mainly due to a process that involves both photodegradation and photochromic reactions; chemical species probably involved in this phenomenon are quinol and phenylcoumaran residues (belonging to lignin impurity).

2.2. Dyeings performed with direct dyes

Dyeing tests were carried out on cotton fabrics (UV irradiated and not) using Solophenyl® (Huntsman) direct dyes for cellulosic fibers applied on 0.1% o.w.f. (on the weight of fabric), 1:40 material to liquor ratio, with 2.0 g/L Albatex UNI as leveling agent, and 1.0 g/L NaCl. The dyeing was performed at 100°C for 30 min, then the samples were cooled at 80°C, and maintained at 80°C for 15 min. The irradiation conditions were the same as reported in Section 2.1.

The final bath exhaustion was about 70% for all the dyes, and the resulted dyeings showed good color level and chromatic homogeneity. However, the color differences between UV-treated and untreated fabrics were minimal, as shown in **Table 2**, where a color difference greater than 5.0 Δ*E* units was evidenced only with Navy Solophenyl BLE, evidenced in bold.

Increasing the dyeing depth over 0.1%, the chromatic differences between UV-treated and untreated fabrics would increase; however, the wet fastness of dyed cotton fabric would be less, then not acceptable. Therefore, this dye selection seems not to be suitable for the differential dyeing.

Dye	Δ*L*	Δ*a*	Δ*b*	Δ*E*
Orange Solophenyl TGL 182%	0.58	−1.0	−1.20	1.68
Bordeaux Solophenyl 3BLE	1.20	−0.75	0.52	1.51
Blue Solophenyl FGLE 220%	1.30	0.75	2.30	2.75
Navy Solophenyl BLE 250%	4.94	0.06	3.58	**6.10**

Table 2. Color difference parameters for 0.1% dyeings with Solophenyl dyes.

On the other hand, differential dyeing effects can be pursued applying UV irradiation on dyed samples, just using the discoloration induced by radiation. In this case, the fading ability of the dyes on cotton yarn was exploited and in many cases significant color differences (Δ*E* higher than 5.0) were found between UV-irradiated and untreated samples.

2.3. Differential dyeing performed with UV fading of reactive dyes

Fading of dyed cotton yarns was carried out on dyed yarn samples wrapped on cardboard where one side was exposed for half area to UV rays. The irradiation condition and color evaluation were the same as reported in Section 2.1.

Two series of reactive dyes for cellulosic fibers were investigated, at first reactive dyes namely Kayacelon React® (Nippon Kayaku) and Kemacelon® (Kem Color) having reactive groups belonging to triazinyl betaine (**Figure 1**).

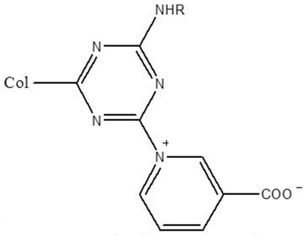

Figure 1. Triazinyl reactive group.

These dyes were applied at 1.0% o.w.f. with liquor ratio of 1:20, in the presence of an alkali donor (1.0 g/L of Buslid 509, which slowly releases hexamethylenetetramine increasing pH) and 40 g/L Na_2SO_4 working at 90°C for 60 min. The results are reported in **Table 3**.

Even this series of reactive dyes presents only a term (Kayacelon React Red CN-3B, evidenced in bold) with acceptable color difference for a differential dyeing between UV-treated and untreated samples.

The chromatic investigation was continued with the reactive dyes Avitera SE® (Huntsman), constituted by a chromogen with three reactive groups (chemical structure still under patent), applied at 0.5% o.w.f., 1:20 liquor ratio, and 50 g/L NaCl working at 60°C for 30 min adding 9 g/L of Na_2CO_3 divided into three aliquots (1/6, 2/6, 3/6), always working at 60°C for another 30 min. The results are reported in **Table 4**.

Dye	Δ*L*	Δ*a*	Δ*b*	Δ*E*
Kayacelon React Yellow CN-RL	−0.18	0.79	−0.48	0.94
Kayacelon React Yellow CN-ML	1.11	−0.49	−0.33	1.26
Kayacelon React G. Yellow CN-GL	−0.02	0.45	−2.43	2.47
Kayacelon React Red CN-3B	2.28	−6.84	2.27	**7.56**
Kayacelon React Blue CN-MG	1.19	0.55	3.68	3.91
Kayacelon React Dark Blue CN-R	3.36	1.78	3.1	4.92

Table 3. Color difference parameters for 1.0% dyeings with Kayacelon React dyes.

Dye	Δ*L*	Δ*a*	Δ*b*	Δ*E*
Avitera Yellow SE	0.86	−0.77	−2.48	2.74
Avitera Red SE	4.92	−10.0	4.02	**11.8**
Avitera deep Blue SE	5.39	4.14	5.06	**8.47**

Table 4. Color difference parameters for 0.5% dyeings with Avitera dyes.

This series of reactive dyes presents only two terms, evidenced in bold, with acceptable values for differential dyeing effects. It was then decided to consider other series of DyStar reactive dyes, based on the monochloro-difluoro-pyrimidine reactive group, Levafix type (**Figure 2a**), and β-sulfatoethylsulfonic reactive group, Remazol type (**Figure 2b**).

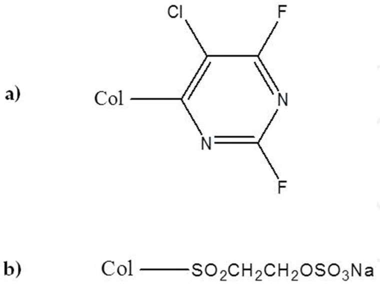

Figure 2. Molecular structure of dyes with monochloro-difluoro-pyrimidine reactive group (a) and β-sulfatoethylsulfonic reactive group (b).

In accordance with the works carried out by Batchelor et al. [24] about photofading, it was observed that light fastness (and therefore also the fading ability toward UV radiations) is instead related to the chemical structure of the chromogen; they showed that fading is caused by both visible and UV light, with visible light responsible for azo dyes and UV light responsible for phthalocyanines.

Generally speaking, the photofading is mainly due to singlet oxygen development, $^1O_2$, which can be formed by the quenching of excited states of dyes by the triplet ground state of oxygen, $^3O_2$:

$$\text{dye} \xrightarrow{\text{light}} \text{dye}^* + {}^3O_2 \xrightarrow{\text{quench}} \text{dye} + {}^1O_2$$

Color index	Commercial name	Light fastness (1/6 SD)	Structure	Reactive group
R.Y. 160	Yellow br. Remazol 4GL	5	Azo	Vinylsulfone
R.Y. 176	Yellow Remazol 3RS	5	Unknown	Unknown
R.O. 107	G. yellow Remazol RNL 150%	4/5	Azo	Vinylsulfone
R.O.16	Orange br. Remazol 3R spec.	4/5	Azo	Vinylsulfone
Unknown	Scarlet Levafix CA	4	Azo	Triazinyl + vinylsulfone
Unknown	Red Levafix CA	4	Azo	Triazinyl + vinylsulfone
R.R. 180	Red br. Remazol F-3B	3/4	Azo	Vinylsulfone
R.Bl. 21	Turquoise Remazol G 133%	5	Phthal.	Vinylsulfone
Unknown	Navy Levafix CA	3/4	Azo	Triazinyl + vinylsulfone
R.Bk. 5	Black Remazol B 133%	3/4	Disazo	2 vinylsulfone
Unknown	Yellow Remazol RR	4	Unknown	Unknown
Unknown	Orange Remazol RR	4	Unknown	Unknown
Unknown	Red Remazol RR	4	Unknown	Unknown
Unknown	Blue Remazol RR	4	Unknown	Unknown
R.Y. 217	Yellow Avitera SE	5/6	Unknown	3 reactive groups
R.R. 286	Red Avitera SE	4	Unknown	3 reactive groups
R.Bl. 281	Deep blue Avitera SE	4	Unknown	3 reactive groups
Unknown	Blue Farbofix SP-BRF 150%	4/5	Unknown	Unknown
Unknown	Navy Farbofix SP-BRK/N	3/4	Unknown	Unknown
R.Bl. 225	Navy Levafix E-BNA	2/3	Unknown	Unknown
Unknown	Blue br. Neareafix AC-BRF 150%	5	Unknown	Unknown

Table 5. Light fastness, structure, and groups of commercial dyes experimented.

Table 5 shows light fastness and structure types of the investigated reactive dyes (data derived from color charts of the producers).

Table 6 shows the measured color differences between UV-irradiated and untreated cotton yarns of the dyeings carried out with 0.5% Levafix dyes, while **Table 7** reports those obtained with 0.5% Remazol dyes (in both tables ΔE > 5 are evidenced in bold).

Dye	**ΔL**	**Δa**	**Δb**	**ΔE**
Levafix Yellow CA	−0.65	−0.36	−3.94	4.01
Levafix Amber CA	2.09	−3.27	−4.98	**6.31**
Levafix Scarlet CA	4.02	−3.80	−1.12	**5.64**
Levafix Red CA	4.37	−5.21	3.15	**7.49**
Levafix Rubin CA	3.05	−4.66	0.42	**5.58**
Levafix Blue CA	1.77	−0.42	4.69	**5.03**
Levafix Navy CA	4.47	2.61	4.35	**6.76**

Table 6. Color difference parameters for 0.5% dyeings with Levafix dyes.

Dye	**ΔL**	**Δa**	**Δb**	**ΔE**
Remazol Yellow br. 4GL	−1.05	0.99	−1.33	1.96
Remazol Yellow RR	−0.17	−0.10	−0.53	0.56
Remazol Orange RR	3.05	−5.94	−5.63	**8.93**
Remazol Red RB 133%	4.65	−11.50	3.69	**12.90**
Remazol Red RR	9.62	−13.17	4.10	**16.80**
Remazol Red 3BS 150%	3.39	−7.62	2.33	**8.66**
Remazol Blue RR	6.50	2.40	5.21	**8.67**
Remazol Navy GG 133%	2.77	3.90	2.83	**5.56**
Remazol Black B 133%	4.58	2.76	4.76	**7.16**

Table 7. Color difference parameters for 0.5% dyeings with Remazol dyes.

Specifically, it was noted that the chromogens more difficult to fade under UV radiations are those providing yellow shades, typically made up of pyrazolone. Only the amber tone (Levafix) is interesting as a yellow, but it is an orange yellow; the fading ability increases going from orange shades (azo) toward red (azo), while in the case of shades provided by diazo dyes the fading ability increases going from navy until the maximum value in the case of Remazol Blue RR, as demonstrated in **Table 7** (Remazol dyeings).

A selection of dyes sensitive toward UV-generated fade was thus performed offering a combination of the six terms reported in **Table 8**.

Dye	**ΔE**
Levafix Amber CA	**6.31**
Remazol Orange RR	**8.93**
Remazol Red RB 133%	**12.90**
Remazol Navy GG 133%	**5.56**
Remazol Black B 133%	**7.16**
Remazol Blue RR	**8.67**

Table 8. Total color difference (ΔE) for 0.5% selected dyeings.

It is possible to observe, as reported in **Tables 6** and **7**, that the total color difference (ΔE) is due not only by an achromatic fading (ΔL) but also results from a variation of chromatic parameters (Δa and Δb), because a tone change after UV exposure occurs.

The selection shown in **Figure 3** has characteristics of good mutual combinability and synchronism in dye exhaustion, together with a color difference higher than 5.0 units of ΔE.

Figure 3. Dyeings with 0.5% selected dyes: (a) Levafix Amber CA, (b) Remazol Orange RR, (c) Remazol Red RB 133%, (d) Remazol Navy GG 133%, (e) Remazol Black B 133%, (f) Remazol Blue RR (for each shade: untreated yarn on the left side, UV faded on the right side).

In conclusion, on cotton fibers, unlike wool, a UV pretreatment does not substantially change the dyeing affinity, but a UV posttreatment is capable to fade dyeing, allowing to obtain interesting differential chromatic effects.

3. Surface modification of cotton fabrics by UV curing and UV grafting

Cotton fabrics often find its application in producing home furnishing, such as table linen, clothing, or work wear with high hygienic requirements. The high concentration of hydroxyl groups on cotton fabric surface makes the fabrics water adsorbent and easily stained by liquids. Moreover, the chemical composition and morphological properties of cellulosic fibers provide an excellent medium for bacterial growth. To overcome these limits, a finishing treatment is required on cotton fabrics to confer oil and/or water repellency and antibacterial activity.

Usually, the desired properties are achieved by thermal polymerization, regardless of energy consumption and costs of the process [25]. Fluorinated or silicone monomers, applied to the fabrics by padding, can confer oil and water repellency, while Triclosan, quaternary ammonium salts, and silver ions [26] are commonly used as antibacterial agents [27].

Ferrero et al. [3] proposed the UV curing as eco-friendly and cheap alternative to thermal curing of functional monomers onto cotton fibers. In UV-curing processes, a suitable photoinitiator is able to interact with UV radiations yielding radical or cationic species, which induce a rapid curing of reactive monomers and oligomers at low temperature, with lower environmental impact and lower cost than thermal process.

For textile applications on cotton fabrics, if a mixture of monomer and initiator is absorbed by the fibers and subsequently UV-irradiated, the polymeric chains can form inside the textile structure, establishing also graft bonds (UV grafting) with the cellulose macromolecules and making the treatment solid and water resistant. Moreover, the interpenetration of components and homogeneous distribution of monomers, even at a low concentration, contribute to obtain textile materials with modified surface properties without high add-on of polymer. In this way, the bulk properties of the fibers, such as mechanical and thermal resistance, are not affected and also the fabric breathability can be kept unvaried.

3.1. Water- and oil-repellent finishing of cotton fabrics by UV radiation

Water and oil repellency are among the most common functional properties that need to be assessed for protective clothing. This property can be conferred by the modification of the surface energy of textile fibers, possibly confined to a thin surface layer, so that the bulk properties of the textile fabric such as mechanical strength, flexibility, breathability, and softness should remain uncompromised.

Hydrophobic or oleophobic surfaces are difficult to wet by water or apolar liquids, respectively, and are called low-energy surfaces. Wetting primarily comes from the non-ideality of solid substrates that are both rough and chemically heterogeneous. The surface modification of textile fibers to confer these properties can be achieved by physical or chemical methods or by the combination of both. Plasma treatments and exposure to radiations, often accomplished in the presence of reactive gases or after impregnation with suitable chemicals, are mainly representative of physical methods, while chemical treatments can generally be carried out with oxidants or other finishing agents, followed by thermal treatment or by sol-gel techniques.

Polysiloxanes are widely used for textile finishing to impart desirable properties such as softness, crease resistance, and water repellency, depending on the nature of organic functional groups incorporated in the polymer structure. The application of a polymeric coating to a cotton fabric in the form of a thin film ensures waterproof properties, but the fabric could lose comfort characteristics, such as handling and breathability. Therefore, hydrorepellency obtained by homogeneous adsorption of monomers onto each fiber and followed by a radiation curing method should be preferred. This was proposed by Ferrero et al. [3], which obtained water-repellent cotton fabrics by radical UV curing of silicone and urethane acrylates. The values of contact angle (**Table 9**), wettability, and moisture adsorption showed that a low resin add-on on the fabric is enough to confer water repellency, while scanning electron microscopy (SEM) analysis confirmed that UV curing yields a coating layer onto each single fiber than a film on the fabric surface (**Figure 4**) without damage of breathability.

Resin	Chemical nature	Weight on cotton (%)	Contact angle (°)
Coatosil 3503	Silicone (medium) acrylate	1.3	143
Coatosil 3509	Silicone (high) acrylate	2.9	114
Tego Rad 2600	Polysiloxane epoxy	2.6	100
Ucecoat 7849	Urethane acrylate (MW = 10,000)	2	100

Table 9. Hydrorepellent finishing of cotton fabrics by radical UV curing of silicone and urethane acrylates.

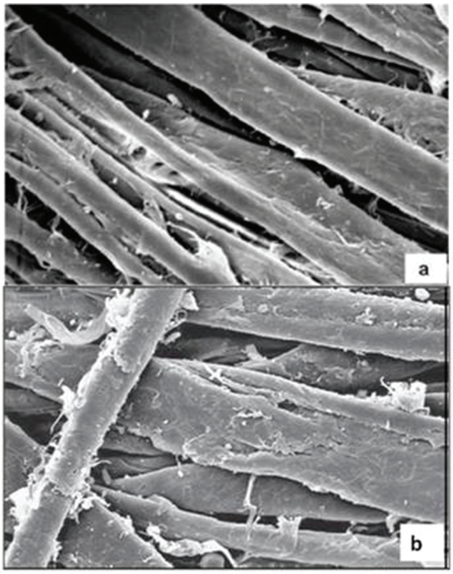

Figure 4. SEM images of cotton fibers untreated (a) and treated by radical UV curing of a silicone acrylate resin 3% add-on (b).

Periolatto et al. [28] recently investigated the application by UV grafting of polyhedral oligomeric silsesquioxanes (POSSs) and a polysilazane (KION 20) to cotton fabrics to confer hydrorepellency.

POSSs are polyhedral clusters yielded by hydrolytic condensation of trifunctional silanes. The generic formula is $(RSiO_{1.5})_n$, where each silicon atom is bound on average to one and a half oxygen atoms and to one hydrocarbon group. The single nanoparticle may be represented as a silica cage core (diameters in the range of 1–3 nm) bearing organic functional groups attached to the corners of the cage (**Figure 5a**).

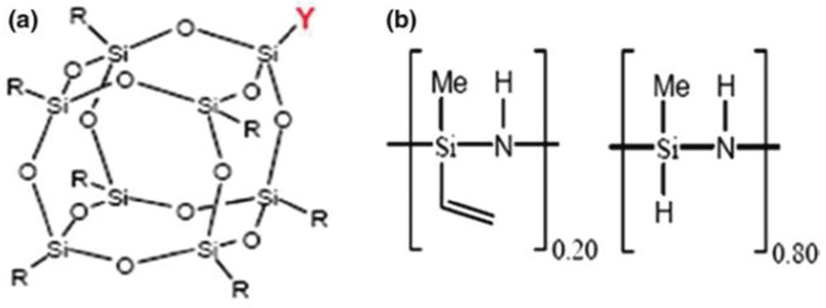

Figure 5. Molecular structures of polyhedral oligomeric silsesquioxanes (POSSs), where R = i-butyl, Y = methacryloisobutyl functional groups (a) and KION 20 structural units (b).

KION polysilazane contains repeating units in which silicon and nitrogen atoms are bonded in an alternating sequence. Both of these units contain cyclic and linear features. In addition, KION 20 contains fewer low-molecular-weight polysilazane components (**Figure 5b**).

For what concerns the hydrorepellency, it was clearly conferred by the treatment, as confirmed by water contact angles measured on the as-prepared samples higher than 90°, for both POSS- and KION-treated samples. Measurements on aged samples revealed that KION-treated samples could maintain better properties during time, with respect to POSS treated. Moreover, for these two oligomers, higher contact angles were measured on samples treated with solutions at higher concentration. In particular, samples treated with 1- and 5-g/L POSS solutions, although showing an initial water contact angle higher than 100°, after aging immediately absorb the water drop, denouncing the total loss of hydrorepellency.

Many research papers have been published on the production and application of different types of fluorochemicals to textile finishing [29]. Fluorochemicals are organic compounds consisting of perfluorinated carbon chains, which impart water and oil repellency to the fiber surface when incorporated into polymer backbone with perfluoro groups as side chains. The old fluorochemicals used were based on C8 carbon chains, which release highly hazardous and toxic substances, such as perfluoro-octanoic acid and perfluoro-octanesulfonates. Nowadays, C6 fluorochemicals are still in use although the rules on this topic became more stringent, banding also C6 fluorochemicals, so studies about the performance conferred by C2–C3 products are of great interest [30].

Fluorochemical finishings are commercially available as water emulsions and are applied to fabrics by the pad-dry-cure method, with a thermal-curing step at 150–175°C in hot flue for some minutes. As alternative, Ferrero et al. [2, 6] proposed the UV curing of perfluoro-alkyl-polyacrylate resins (Repellan EPF and NFC by Pulcra Chemicals and Oleophobol CP-C by Huntsman), in water emulsions, able to impart water as well as oil repellency to cotton fabrics, and the results were compared with those obtained by thermal polymerization. A radical photoinitiator was added in the proper amount, then the solution was diluted with water, mixed, and applied by dipping or spraying onto strips of fabric that were dried in an oven. Final weight add-ons of 3 and 5% o.w.f. were usually applied in order to obtain the desired properties without loss of fabric handling. Then, the samples were UV radiated on both sides by a medium pressure mercury lamp (about 60 mW/cm^2) under inert atmosphere for 30–60 s. Thermally cured fabrics were considered as reference, treated for 2–3 min at 140 or 150°C according to the indications of the producer.

			Contact angle (°)					
			Before washing			**After washing**		
Resin	Add-on (%)	Curing type	θA	θR	Δθ	θA	θR	Δθ
Repellan EPF	3	Thermal	134	126	8	142	136	6
	3	UV	138	129	9	134	131	3
	5	Thermal	145	133	12	143	140	3
	5	UV	142	134	8	138	134	4
Repellan NFC	3	Thermal	140	130	10	139	122	17
	3	UV	140	132	8	137	123	14
	5	Thermal	136	125	9	134	124	10
	5	UV	133	126	7	131	119	12

Table 10. Dynamic water contact angles (average of repeated measurements, standard deviation about 4°, θA = advancing, θR = receding, Δθ = hysteresis) before and after washing on cotton fabrics cured with Repellan EPF and NFC.

The effectiveness of the UV treatment was evaluated by the determination of weight loss in chloroform. Repellan EPF showed the highest yields after UV curing, quite similar to those reached with the thermal treatment (93–96%), whereas Repellan NFC showed lower, although acceptable, yields in UV curing (80–81%) than in the thermal one (98%), without the influence of irradiation time and polymer add-on. However, with Oleophobol CP-C lower yields were obtained in both finishing treatments, and longer UV irradiation time, at least 60 s, is necessary to achieve a yield of 91% with a 3% add-on. Measurements of dynamic contact angles of water and oil drops allowed comparing the repellent behavior of the cotton fabrics finished with both curing methods before and after five domestic washing cycles (**Table 10**). A hysteresis $\Delta\theta > 0$ is typical of most real surfaces, as confirmed by all the results obtained. The good wash fastness of water repellency was proved by the slight reduction of the advancing contact angles after washing, regardless of the curing type and polymer add-on. Oleophobol (data not reported) gave slightly lower contact angles but was practically unaffected by repeated washings.

In conclusion, the laboratory-scale application of the hydro- and oil-repellent finishing on textile fabrics by UV curing of silica based or fluorocarbon resins, with the optimization of process parameters, followed by a deep characterization of treated samples, confirmed the effectiveness of the treatment.

The study of Ferrero and Periolatto went on with the semi-industrial scale-up of the process: a great number (about 80) of larger fabric samples were padded by foulard with Oleophobol and then were irradiated in air by Sun-Wash®, an apparatus for continuous treatment of fabrics by UV light providing an irradiance of 913 mW/cm^2 on an exposed area of about 120 × 60 cm^2. Samples were exposed to the radiation with a carpet speed of 5 m/min, by five passes, corresponding to an irradiation time of 35 s, on both sides [31]. Fabric add-on was significantly reduced in order to hold down the finishing cost. White and dyed samples of different textile composition were treated and evaluated in terms of conferred repellency, yellowing, or color changes. Most relevant process parameters were investigated, considering the thermal process normally adopted at industrial level as reference. Results were so statistically evaluated by Six Sigma method with Minitab 16 software, to point out the most influencing parameters and the real possibility to replace the thermal treatment with UV. Water and oil drop sorption times higher than 2 h were found on all treated samples, showing that Oleophobol works very well as oil- and water-repellent agent for textiles.

UV process was revealed to work better than thermal one, in fact higher water and oil contact angles were obtained with a lower amount (1% o.w.f.) of finishing agent. Considering the UV process, best results were related to white fabrics, rather than dyed, and medium values of both radiation dose and product concentration, taking into account both contact angles and color reflectance evaluations. Finally, contact angle measurements carried out on aged samples (2 years) showed no variations with respect to fresh samples, meaning that the finishing is not affected by aging. Obtained results were considered encouraging and can open the way for a real application of the UV process to industrial field.

3.2. Antimicrobial finishing by chitosan UV grafting

The textile manufacturing industry is going through a period of severe crisis due to the globalization of the world market. A highly competitive context and stringent ecological regulations make quality and eco-friendly processes the major demands for a company.

A first objective aims to lower water and energy consumption; another relevant factor is the possibility of replacing high-polluting or toxic chemicals with others characterized by lower or zero environmental impact. From this point of view, the products of green chemistry, of natural origin, are particularly interesting for applications in the field of textile finishing.

Increased attention toward health and hygiene, due to frequent diseases and invasive infections, brought the attention of the research in textile field on antibacterial materials, which can not only prevent degradation and discoloration of the fabrics by microorganisms but also effectively prevent the spread of pathogenic bacteria. An antibacterial finishing, by means of a suitable surface chemical modification of fibers, is mainly required on natural fibers for furnishing, technical textiles, medical devices, hygienic textiles, food industry, and packaging. Chemicals bearing functional biocide groups are usually applied by padding, followed by a thermal treatment. Unfortunately, most of these products are toxic or carcinogenic, so the application to textiles is not advisable, also considering a possible release of the antibacterial agent during the use, in skin contact.

For these reasons, a strong chemical grafting to treated fibers is mandatory for a fast, stable, and resistant treatment. However, the finishing should not compromise the hand, appearance, and color of the fabric, considering that finishing processes are normally carried out after dyeing. In this view, the application of natural biopolymers by an eco-friendly and cheap process can be the winning choice to develop bioactive eco-sustainable textiles from renewable sources [32].

Cellulose and chitin, the main components of cotton fibers and crustacean shells, respectively, are the two most abundant polysaccharides in nature. They are mutually compatible, due to their similar structure (**Figure 6**), and biodegradable; it makes them good candidates as eco-friendly and eco-sustainable substrates for textile applications. Chitosan (2-amino-2-deoxy-(1–4)-β-D-glucopyranan) is a carbohydrate biopolymer derived from the deacetylation of the chitin with unique biological, physiological, and pharmacological properties, such as biodegradability, no toxicity, and high antibacterial activity toward both Gram-positive and Gram-negative microorganisms, due to the combined bacteriostatic and bactericide action.

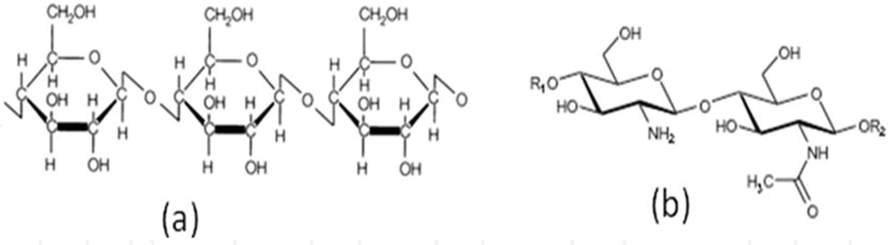

Figure 6. Molecular structures of cellulose (a) and chitosan (b).

In textile field, chitosan is mainly used as a dyeing auxiliary or a finishing agent, but the finishing fastness is limited by the weak interactions between chitosan macromolecules and fibers. To obtain a stable treatment, a thermal wet process is required, with high energy, water consumption, and possible degradation of the treated substrate. Moreover, the addition of cross-linking agents is required. Usually, toxic chemicals bearing aldehyde groups are used in thermal processes; recently, genipin was proposed as natural, nontoxic alternative: encouraging results in terms of fastness improvement were obtained, opening the way for biomedical and pharmaceutical applications [33], but the prohibitive cost of genipin makes it not applicable in textile field.

Ferrero and Periolatto [34] proposed photocuring (UV curing and/or UV grafting) as cheap and eco-friendly process to bind chitosan to textiles by means of radical reactions. Studies about the photodegradation of chitosan macromolecules due to UV exposure confirmed the formation of macroradicals on the polymer. Same radicals can be involved in cross-linking process, promoted by the presence of a suitable radical photoinitiator. Among the substrates considered, there are wool [35], silk [36], polyester, polyamide, and cotton fiber [37], in the form of weft-warp and knitted piquet fabrics [38] but also filter substrates and gauzes with more open structures [39–41].

Focusing on cotton, the research work started with laboratory test on samples of small dimensions, aimed to optimize the process parameters and confirm the treatment efficiency and fastness [36]. A low-viscosity chitosan with deacetylation degree of 75–85% was dissolved in acetic acid solution at pH 4. The solution was added of 2-hydroxy-2-methyl-phenyl-propane-1-one, 4% wt on chitosan, as radical photoinitiator, properly diluted and applied to the fabric surface by dipping, to reach a chitosan add-on ranging from 1 to 3% wt. An impregnation time of 12 h at 25°C or 1 h at 50°C was necessary to obtain 100% process yield.

Chitosan UV curing yielded high antimicrobial properties, against *Escherichia coli* and *Staphylococcus aureus*, on cotton fabrics. The test was carried out according to ASTM E 2149-01 standard test. A microorganism reduction higher than 97% was found on all treated samples, regardless of the application method for chitosan. Moreover, about 2% polymer add-on was enough to confer a strong antibacterial activity to the fabrics without endangerment of hand and breathability. An impregnation time of 12 h at ambient temperature was necessary so that treated fabrics maintained about one half of their own antimicrobial activity after washing with standard ECE detergent, according to UNI-EN ISO 105 C01 standard test, while at lower impregnation time, the antimicrobial activity was more reduced. This was attributed to a not-enough penetration of chitosan inside the fiber structure, due even to the high viscosity of the solution. A prolonged contact time between chitosan solution and fabrics improved this penetration and chitosan could graft to the fibers, showing increased washing fastness. However, this was strongly dependent on the ionic nature of the detergents, and a nonionic surfactant could assure that an antimicrobial activity completely retained after repeated washings.

Semi-industrial scaled tests were carried out on samples of higher dimension, using commercial chitosan powder (Peripret or Chitoclear) dissolved in acetic acid solution [38]. In some cases, a softener (Nearfinish SM/40) or an antioxidant agent (Nearcand) was added to the recipe, while the radical photoinitiator was kept in the same amount. The chitosan add-on was drastically lowered till 0.3% o.w.f, diluting the solution to 0.25% before the impregnation by padding. The as-impregnated samples were dried in a rameuse and finally radiated by Sun-Wash®, as reported in Section 3.1. Results of antibacterial activity tests are reported in **Table 11** and confirmed those previously obtained with samples prepared at laboratory scale.

Sample description	Condition	Microorganism reduction (%)
Untreated		–
Ultrafresh GH-20 2%	Initial	>99.9
	10 washes	>99.9
	30 washes	98.4
Chitosan finishing: 3% Peripret	Initial	>99.9
Wet irradiation	10 washes	>99.9
	30 washes	>99.9
Chitosan finishing 3% Peripret	Initial	>99.9
Dry irradiation	10 washes	>99.9
	30 washes	>99.9
Chitosan finishing: 3% Peripret	Initial	>99.9
With Nearfinish SM/40	10 washes	>99.9
Dry irradiation	30 washes	>99.9
Chitosan finishing: 0.3% Chitoclear	Initial	98.6
Wet irradiation	10 washes	>99.9
	30 washes	>99.9
Chitosan finishing: 0.6% Chitoclear	Initial	99
Wet irradiation	10 washes	>99.9
	30 washes	>99.9
Chitosan finishing: 0.6% Chitoclear	Initial	99.2
With Nearcand	10 washes	>99.9
Wet irradiation	30 washes	>99.9

Table 11. Antibacterial activity of chitosan-treated samples as prepared and after 10 and 30 washing cycles. Quantitative assessment of activity according to ISO 20743: 2007 (E) against *Staphylococcus aureus*.

"*Chitosan conferred a strong antibacterial activity, with the total reduction of the microorganism colonies on all the tested samples. Moreover, chitosan treated samples showed optimum washing fastness, maintaining their antibacterial activity unvaried even after 30 washes*" [38]. Comparing the results with those related to Ultra-Fresh, a commercial sanitizing agent considered as reference, the performances are similar or even better for chitosan-treated samples after 30 washes. Obtained results are of particular interest considering that the UV exposure was carried out in the presence of oxygen, even on wet samples. "*These are generally considered unfavorable conditions for radical reactions occurring or for photoinitiator effectiveness. Moreover, the strong antibacterial activity and washing fastness were obtained on all treated samples regardless the add-on or the presence of additives* [38]."

"Results obtained with the lowest amount of chitosan on fibers is particularly interesting because makes chitosan competitive with other antibacterial agents commonly used, such as Triclosan, silver ions or quaternary ammonium salts, even from an economical point of view" [38]. The homogeneous distribution of chitosan on fabrics, in particular in correspondence to the sample that presented the best fastness, was confirmed by dyeing tests with an acid dye (**Figure 7**) and by SEM analysis (**Figure 8**) that showed the optimal distribution of the finish on a single fiber surface.

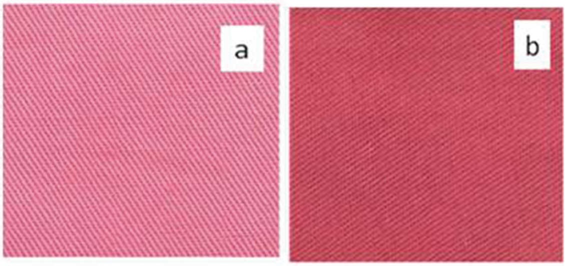

Figure 7. Dyeing test with Direct Red 81: untreated cotton fabric (a), treated with 0.6% wt. chitosan (Peripret CTS) (b).

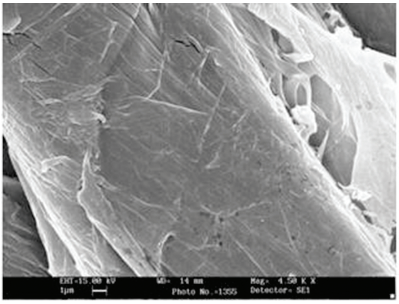

Figure 8. SEM analysis on cotton fabric treated with 3% wt. chitosan (4500×).

4. Conclusion

The UV treatments on cotton fibers can be utilized in dyeing and finishing processes. UV irradiation coupled with mild oxidation can improve some properties of the cotton fibers such as pilling resistance, water swelling, and dyeability. However, significant effects of differential dyeing were obtained by a UV posttreatment capable to fade dyeings with reactive dyes. UV curing and UV grafting with suitable chemical enabled to modify the surface of cotton fibers in order to confer oil and/or water repellency with an eco-friendly and cheap alternative to chemical and thermal finishing treatments. Moreover, the chitosan UV grafting was proposed as valid environmental friendly method to obtain cotton fabrics with a satisfactory washing-resistant antimicrobial activity even with low polymer add-on.

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