

Water-Repellent Finishing of Cotton Fabrics by Ultraviolet Curing

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ABSTRACT: Cotton fabrics were water-repellent-finished by radical ultraviolet curing of silicone and urethane acrylates with different formulations. The fabrics were impregnated with undiluted resins and with toluene solutions or water emulsions. Moreover, cationic ultraviolet-curable systems were also investigated, such as an epoxy-functional polysiloxane and mixtures of an epoxy resin with hydroxyl-containing silicone additives. The gel content and polymerization yield were considered for the ultraviolet-curing process evaluation. Water-resistance properties

were determined in terms of the contact angle, wettability, moisture adsorption, and water vapor permeability measurements, whereas the morphology and surface composition of treated fabrics were examined with scanning electron microscopy and energy-dispersive X-ray analysis. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 810–818, 2008

Key words: cationic polymerization; photopolymerization; radical polymerization; silicones

INTRODUCTION

Radiation processes have several commercial applications in the coating of metals, plastics, and glass, in printing, in wood finishing, in film and plastic crosslinking, and in the fields of adhesives and electrical insulation.¹ The advantages of this technology are well known: energy savings (no drying and a low-temperature process); low environmental impact (no solvent emissions); simple, cheap, and small equipment; and a high treatment speed. Despite these advantages, there have been few applications of radiation curing in the textile industry, such as nonwoven fabric bonding, fabric coating, and pigment printing.^{1–3} In fact, in textile finishing processes, the conventional thermal curing technique is still used, regardless of energy consumption and cost. Among the textile finishing processes by radiation curing, pigment printing of fabrics has received much attention,^{4,5} but coatings for shrink-resistant wool,^{6,7} flame-retardant fabrics,⁸ and durable press finishes⁹ have also been investigated. Moreover, water-repellent fabrics have been obtained by the γ -radiation grafting of poly(vinyl methyl siloxane) or methyl hydrogen silicone¹⁰ on hydrophilic substrates. In industrial applications, ultraviolet (UV) light from a mercury vapor lamp is preferred for

thin coatings because of the high efficiency of energy absorption and low equipment cost.

Polysiloxanes are widely used for textile finishing to impart desirable properties such as softness, crease resistance, and water repellency. Waterproof and water-repellent finishes are required in particular for cotton fabrics. However, the specific properties conferred by siloxanes depend on the nature of the organic functional groups that are incorporated into the polymer structure.¹¹ The choice of a silicone instead of other organic coatings is based on its unique properties and performance, such as flexibility at low temperatures, excellent heat and cold resistance, good weathering performance, water repellency, and good electrical properties. Thermal crosslinking of polysiloxanes by chemical-initiated methods involves the use of organic solvents, unsaturated compounds containing silanol groups, and a high temperature, whereas in UV curing, radical or cationic species are generated by the interaction of UV light with a suitable photoinitiator, which induces the curing reaction of reactive monomers and oligomers at a low temperature. Moreover, urethane acrylate resins have also been tested for the UV curing of fabrics to improve the mechanical properties.¹²

The application of a polymeric coating to cotton fabric ensures good homogeneity of conferred properties, but the fabric could lose comfort characteristics, such as handling and breathability. If a monomer and initiator mixture is adsorbed onto the fibers and subsequently UV-cured,¹³ the polymeric chains

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TABLE I
Properties of Silicone and Urethane Acrylate Resins

Resin	Chemical nature	Density (g/cm ³)	Viscosity (mPa s)	Water solubility	Flash point (°C)
CoatOSil 3503	Silicone (medium) acrylate	1.03	1030	Dispersible	300
CoatOSil 3509	Silicone (high) acrylate	1.03	1290	Insoluble	300
CoatOSil 2810	Polysiloxane epoxy	0.99	—	Insoluble	99
TEGO Rad 2600	Silicone acrylate	0.98	700–1100	Insoluble	—
UCECOAT 6558	Urethane acrylate (molecular weight = 2000)	1.09	<4500	Water solution (49–51% solid)	—
UCECOAT 7849	Urethane acrylate (molecular weight = 10,000)	1.02	<200	Water dispersion (34–37% solid)	—

can form inside the textile structure, which can also establish graft bonds, making the treatment solid and water-resistant. Moreover, the interpenetration of components and homogeneous distribution of monomers, even at a low concentration, contribute to obtaining textile materials with modified surface properties without high add-on of the polymer, which is present in a small amount.

In this work, cotton fabrics were water-repellent-finished by radical UV curing of silicone and urethane acrylates with different formulations. Moreover, cationic UV-curable systems were also investigated, such as an epoxy-functional polysiloxane and mixtures of an epoxy resin with hydroxyl-containing silicone additives. The water-resistance properties were determined in terms of measurements of the contact angle, wettability, moisture adsorption, and vapor permeability, whereas the morphology and surface composition of treated fabrics were examined with scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis.

EXPERIMENTAL

Materials

The used fabric was plain-weave pure cotton (133 g/m²) previously washed but not subjected to any finishing processes. This material presented a zero contact angle; in fact, a water drop was soon adsorbed because of the greatly hydrophilic behavior of cotton.

The silicone fluids used in this investigation were CoatOSil 3503 and CoatOSil 3509, which are silicone acrylate polyether copolymers for radiation-cured coatings, and CoatOSil 2810, a polysiloxane diglycidyl ether; the products were supplied by OSi Crompton Europe (Geneva, Switzerland). Moreover, TEGO Rad 2600, a crosslinkable silicone acrylate release additive, was supplied by Degussa Goldschmidt UK (Kingston, UK). UCECOAT 6558 and UCECOAT 7849, water-based aliphatic urethane acrylates, which were supplied by Cytec Industries (West Paterson, NJ), were also investigated. The

physical properties of these materials are reported in Table I.

Among the cationic UV-curable systems, besides CoatOSil 2810, the epoxy resin Araldite DY-T (triglycidyl ether of trimethylolpropane), supplied by Ciba Specialty Chemicals (Origgio, Italy), was used with BYK silicone hydroxyl-ended additives supplied by BYK Chemie (Wesel, Germany). In particular, BYK 370, BYK 373, and BYK 375 are solutions of a polyester or polyether modified hydroxyl-functional polymethylsiloxanes, but BYK 373 has a content of hydroxyl groups higher than the others. BYK Silclean 3700 is a solution of hydroxyl-functional, silicone-modified polyacrylate.

To obtain a more homogeneous distribution of resins on the fabrics, toluene (99%; Aldrich, Milano, Italy) was used as a solvent, whereas a nonionic surfactant, Tergitol NP14 (Union Carbide, Danbury, CT), was used as a emulsifying agent for water-based mixtures.

Darocure 1173 (Ciba Specialty Chemicals) was used as a radical photoinitiator, whereas Cyacure UVI 6974 (a mixture of sulfonium salt at 50 wt % in propylene carbonate, kindly supplied by Dow, Midland, MI) and TEGO 1465 (iodonium salt, kindly supplied by Degussa) were used as cationic photoinitiators. The iodonium salt was soluble in silicone resins.

UV photopolymerization

The formulation was first prepared by the dissolution of the photoinitiator in the resin in the proper amount (4% w/w) to produce a film with each system considered. In some cases, to achieve a more homogeneous spread of the liquid resin on cotton, toluene or a surfactant aqueous solution was added as a diluent to the mixtures, with continuous stirring until complete homogeneity was obtained. The formulation was then applied with a glass stick onto the surface of strips of fabric having fixed dimensions of 5 × 2.5 cm². With diluted formulations, fabrics were then left in air in the case of toluene or in an oven at 90°C in the case of a water emulsion for some minutes to evaporate the solvent. The quantity

of resin put on the fabrics was adjusted according to the desired weight percentage.

The surface-coated fabrics were exposed to UV radiation with a medium-pressure mercury lamp with a light intensity on the fabric of about 20 mW/cm² in a small box equipped with a quartz window under a nitrogen atmosphere (oxygen content < 20 ppm). The required radiation dose was obtained by the adjustment of the distance of the textile from the lamp and the exposure time.

Gel content and yield of the process

A resin solution is adsorbed by a textile, so the polymerized structure should not form a surface coating but should penetrate the cotton fibers. To test if UV radiation was effective even inside the cotton and if the adsorbed monomer was completely polymerized, the gel content was measured. This was determined on the cured fabrics by the measurement of the weight loss after 24 h of extraction with chloroform at room temperature, followed by solvent evaporation in an oven at 90°C for 1 h. The yield of the process was estimated by a comparison of the amount of the resin polymerized on the textile with the initial weight of the resin deposited on the same. It differed from the gel percentage because, particularly for diluted resins, a part of the monomer was lost by evaporation with the solvent and in the radiation room.

Contact-angle measurements

The surface properties of treated and untreated textiles were tested by optical measurements of the static contact angle of water drops on the textile surface. This gave values as higher as the hydrophobic behavior of the textile was greater. Measurements were carried out on a Krüss (Hamburg, Germany) DSA 10 instrument equipped with a video camera, and the contact angles were estimated with the four methods available with the instrument software, but only the fitting method that used the Young–Laplace equation was considered for comparison. The measuring liquid was high-performance liquid chromatography (HPLC) grade water.

Wettability measurements

The wettability of various weighed cotton samples were measured at 23°C with a Krüss K100 SF tensiometer (single fiber), which, because of its great sensitivity, allowed a reliable determination of the surface characteristics of the textiles and single fibers. The instrument was connected to a personal computer, and the data were collected and processed with Lab-Desk software.

Small pieces of treated and untreated cotton, about 2 mm wide and 0.5 mg in weight, were fixed with a clamp to a probe connected to a high-precision microbalance. Under the probe, a glass vessel was placed containing the liquid required for the test, which was slowly brought to the sample. The balance recorded the weight increase during the immersion time, and the data were stored for further calculations. To determine the capillary constant, which characterizes the wickability of the fabric, a liquid with a zero contact angle is necessary, which enables the constant to be calculated from the slope of the straight line obtained by the plotting of the initial values of the squared weight of the sample versus time. For this purpose, *n*-hexane was chosen, whereas for wettability evaluations, HPLC-grade water was used.

Moisture adsorption and vapor permeability evaluation

Treated and untreated cotton fabric samples were previously dried in an oven at 80°C for 24 h and weighed. Then, they were left suspended in a closed chamber over a NH₄H₂PO₄ saturated solution for 24 h and weighed again to determine the water amount adsorbed by each one. This ambient condition provided a 93% relative humidity atmosphere at 23°C.

The determination of the vapor permeability of finished fabrics was evaluated according to DIN 52615. In fact, the procedure can be applied to homogeneous, fibrous, or porous materials and even to multilayer composites. In a glass flask, a constant partial pressure of water vapor was maintained by the introduction of a weighed amount (5 g) of anhydrous CaCl₂, a highly hygroscopic salt. The flask was sealed with the testing weave and put in a glass chamber with a saturated solution of NH₄H₂PO₄ to obtain a controlled atmosphere with 93% relative humidity at 23°C. 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, the weight of the flask being recorded once a day.

SEM and EDX analysis

The surface morphology of the fabrics was examined by SEM with a Leica (Cambridge, UK) Electron Optics 135 VP scanning electron microscope with an acceleration voltage of 15 kV, a current probe of 400 pA, and a working distance of 20 mm. The samples were mounted on aluminum specimen stubs with double-sided adhesive tape and sputter-coated with gold in rarefied argon with an Emitech (Kent, UK) K550 sputter coater with a current of 20 mA for 180 s.

TABLE II
Results of UV Curing of Cotton Fabric with Silicone Acrylate Resins

Resin	Irradiation time (s)	Diluent	Weight on cotton (%)	Gel content (%)	Yield (%)	Contact angle A (°) ^a	Contact angle B (°) ^b
CoatOSil 3503	45 (one side)	None	24.5	95.9	72.5	121.7	81.7
	45 (each side)	None	23.8	90.5	76.4	88.5	73.7
	45 (each side)	Toluene (1 : 4)	3.1	63.8	63.8	103.2	52.0
	45 (each side)	Toluene (1 : 2)	2.5	89.4	69.4	99.6	91.7
	45 (each side)	Tergitol (0.05 g/L)	1.3	89.7	17.0	143.0	140.2
	45 (each side)	Tergitol (0.05 g/L)	9.9	99.4	38.7	127.4	120.0
	45 (each side)	Tergitol (1 g/L)	17.2	95.1	63.4	154.3	110.9
	45 (each side)	Tergitol (1 g/L)	40.3	93.6	97.5	132.2	131.0
CoatOSil 3509	45 (one side)	None	21.3	91.2	81.3	109.6	98.0
	45 (each side)	None	22.5	87.7	80.5	85.2	74.5
	45 (each side)	Toluene (1 : 4)	3.2	89.7	53.0	97.3	84.0
	45 (each side)	Tergitol (1 g/L)	2.9	74.1	76.9	113.5	108.3
	45 (each side)	Tergitol (1 g/L)	2.7	66.7	65.7	—	—
TEGO Rad 2600	45 (one side)	None	24.1	95.6	89.5	98.2	93.1
	45 (each side)	None	20.1	94.2	82.5	92.4	85.0
	45 (each side)	Toluene (1 : 4)	2.6	94.3	48.1	100.0	94.9

^a On the side on which the resin was spread.

^b On the opposite side.

EDX analyses were performed on an Oxford Instruments (High Wycombe, UK) model 7060 Link ISIS interfaced to a personal computer using 4096 channels in the range of 10 keV, with a preset integral of 16,000 counts between 0.00 and 3.00 keV. X-ray microanalysis was performed with a dead time of about 25%, a 400-pA probe current, a 15-kV accelerating voltage, and a 20-mm working distance.

RESULTS AND DISCUSSION

Radical photopolymerization

At first, the polymerization conditions were tested to produce a polymeric film on a poly(ethylene terephthalate) substrate. A concentration of 4% Darocure 1173 as a photoinitiator and 45 s of irradiation time in an inert atmosphere were found necessary to obtain a solid film with all the resins suitable for radical photopolymerization. Then, the weighed cotton samples were impregnated with pure resin, resin diluted with toluene, or resin emulsified with a surfactant solution. In the last case, the resin was emulsified with a magnetic stirrer and then spread on the fabric. In fact, the high viscosity of the resins made its homogeneous distribution on the fabric difficult.

The results obtained with silicone acrylate resins are reported in Table II. Static contact angles with a fitting method were evaluated on both sides of the fabric; A was the side on which resin was spread, and B was the opposite one. High values of the gel percentage were found, not depending on irradiation on just one or both sides but with a little decrease by dilution of the monomeric mixture. The process

yields were generally high, with a low decrease if the resin was diluted and a higher one at a low resin content, but already a low weight percentage had a strong effect on the increase in the contact angle. The very good result of the treatment was confirmed by a strong hydrophobic behavior, with poor differences between the two sides of the fabric. Hence, the polymer should not have formed a coating layer on the surface of the textile, but the monomeric mixture was adsorbed inside the fabric and *in situ* polymerized.

However, although in the case of dilution with toluene there was great homogeneity on the surface, with a high contact-angle measured everywhere, zones with high and zero contact angles were found with emulsions, as confirmed by the results obtained with CoatOSil 3503. This might have happened because the monomer was not emulsified so well and the deposition on the textile was in lumps.

The preparation of an emulsion in a great amount with vigorous mixing did not increase homogeneity, although the yield of the process was higher. However, samples with the highest weight increase were a bit rigid and showed a pale yellow color, whereas the lower weight ones did not differ from untreated cotton in aspect but showed great water-repellency properties according to the contact-angle measurements.

Solvent-free systems are generally preferred in industrial applications because of pollution problems. Searching for an alternative to toluene, we considered two UCECOAT water-based resins, emulsion 7849 and suspension 6558. Both resins are suitable for radical UV curing, so Darocure 1173 as a photoinitiator and irradiation under inert atmosphere are required.

TABLE III
Results of UV Curing of Cotton Fabric with UCECOAT Urethane Acrylate Resins

Resin	Irradiation time (s)	Diluent	Weight on cotton (%)	Gel content (%)	Yield (%)	Contact angle A (°) ^a	Contact angle B (°) ^b
6558	180 (each side)	Water	3.4	93.9	54.8	—	—
6558	180 (each side)	Water	19.5	97.4	87.2	—	—
7849	180 (each side)	None	12.2	95.1	19.4	82.5	59.3
7849	180 (each side)	Water	2.0	83.3	40.3	100.2	97.0
7849	180 (each side)	Water	16.1	89.2	74.3	93.5	68.3

^a On the side on which the resin was spread.

^b On the opposite side.

In this case, the production of a film needs a previous treatment of the spread resin in an oven at 90°C for 5 min to eliminate water, 4% Darocure 1173, and 3 min of irradiation. The dilution to improve the spreading homogeneity on cotton can be made in this case simply with water, and the spread cotton needs heating in an oven to remove water before irradiation.

Contact-angle measurements on film showed high values for the emulsion and very low values for the suspension, so it can be supposed that only the first one gave hydrophobic properties to cotton. In Table III, high values of the gel percentage but lower yields are shown by both products, as in the case of toluene dilution with silicone resins. This could happen because some of the monomer was lost during water elimination. As suspected, the contact-angle measurements provide evidence of the good effect of UCECOAT 7849 on the hydrophobic properties of cotton, even at a low polymer concentration, whereas the cotton treated with UCECOAT 6558 immediately adsorbs the water drop. On the other hand, this resin remains water-soluble even after UV curing and should be unsuitable for a permanent treatment. As for the aspect of treated textiles, the fabrics have soft hand, above all at a low polymer concentration, and the treatment seems generally homogeneous on the fabric surface without yellowing.

Cationic photopolymerization

The use of a cationic process is very interesting because it does not need an inert atmosphere in the irradiation room; this removes possible problems for an industrial application. A CoatOSil 2810 polymeric film was obtained with 4% Cyracure UVI 6974 or 1% iodonium salt as a photoinitiator with 75 s of irradiation. In the first case, photopolymerization did not occur in the presence of solvents, whereas in the latter, it occurred in any case.

In all the tests on cotton, the results of which are reported in Table IV, low gel percentage and yield values were found with Cyracure and with iodonium salt, although the latter should be more effi-

cient because of its solubility in silicone resins. The gel percentage and yield did not increase with increasing irradiation time or with irradiation on both sides. For some treated cotton, the gel percentage was measured after 24 h to allow the polymerization process to go on even after irradiation, but the results did not significantly increase.

Another epoxy monomer investigated was Araldite DY-T, which on its own does not confer water repellency to fabric. At first, a polymeric film from Araldite was obtained with a cationic process, with 4 wt % Cyracure as a photoinitiator and 75 s of irradiation. The second step was the impregnation of cotton with Araldite, which could be made easy with acetone, a solvent with less environmental impact than toluene, to dilute the monomer for a low weight. Finally, after irradiation of both the sides of the fabric, a gel percentage of 83% and a yield of 79% were found with a weight of 60% on cotton. The differences between the gel percentage obtained with CoatOSil 2810 and Araldite could be justified by the higher crosslinking density of the Araldite network due to the trifunctional epoxy monomer, whereas CoatOSil 2810 is a difunctional epoxy polysiloxane.¹⁴

Water-repellent effects can be obtained by the mixing of Araldite with reactive additives such as BYK silicone-modified reagents with hydroxyl-functional groups. In fact, hydroxyl-containing additives are

TABLE IV
Results of UV Curing of Cotton Fabric with CoatOSil 2810

Irradiation time (s)	Diluent	Weight on cotton (%)	Gel content (%)	Yield (%)
75 (one side) ^a	None	0.6	2.0	1.9
75 (each side) ^a	None	0.8	2.9	2.7
75 (each side) ^a	Toluene	0.4	14.9	6.8
75 (one side)	Toluene	0.4	10.3 ^b	7.2
180 (one side)	Toluene	0.5	16.7 ^b	10.8
240 (one side)	Toluene	0.3	9.8 ^b	4.8

^a These samples were obtained with Cyracure UVI 6974 as a photoinitiator; the other samples were obtained with TEGO 1465 iodonium salt.

^b Measured the day after the polymerization.

TABLE V
Contact Angles of Water on UV-Cured Films of Araldite DY-T with BYK Additives at Different Weight Percentages After an Irradiation Time of 75 s

BYK 370 (%)	Contact angle (°)	BYK 373 (%)	Contact angle (°)	BYK 375 (%)	Contact angle (°)	Silclean 3700 (%)	Contact angle (°)
0	63	0	63	0	63	0	63
1.6	103	2.2	81	1.6	90	1.5	86
—	—	5.4	95	5.2	92	4.9	90
7.4	95	7.3	91	7.3	91	6.9	91
10.4	102	11.3	91	10.2	97	10.0	92
20.2	93	28.8	99	21.1	89	20.0	92

known to interact with the carbocationic growing chain through an activated monomer mechanism.¹⁵ The final result is the presence in the polymeric network of additive moieties. Moreover, it was reported in a previous investigation¹⁶ that hydroxyl-containing silicone additives were able to deeply modify the surface properties of an epoxy-based coating.

The investigation began with the production of Araldite films with an increasing percentage of additives. The contact angles of water on these films were measured, and the results are shown in Table V. A high increase in the contact-angle values given by the presence of additives was observed, even at a low percentage, in comparison with the Araldite alone because of the positive effect of the silicone chain involved in the epoxy polymer. The results show that the contact-angle values do not increase linearly with the percentage of the additive, but higher values than those with pure Araldite are evident.

After the study of polymeric films, the investigation continued by the application of the polymeric mixtures to cotton, which was followed by an evaluation of the gel percentage and contact angle. BYK 373 and BYK Silclean 3700 at 5% and 20 wt % on Araldite with different weights on cotton were tested: photopolymerization occurred under same conditions used for pure Araldite. Similar effects were supposed with the other additives. However, contact-angle measurements on cotton treated with Araldite only or with 5% additive were impossible because the water drop was instantaneously adsorbed, whereas on cotton treated with Araldite plus 20% additive, the drop was persistent and well shaped, with a contact-angle value typical of hydrophobic materials. The results of Table VI show that the same additive content yielded satisfactory gel percentage values with a decrease at lower weight percentages.

Wettability measurements

At first, untreated cotton and some differently treated fabrics were subjected to capillary constant measurements with a Krüss K100 SF tensiometer.

Details of the samples and measured capillary constant values are reported in Table VII. The treated fabrics showed capillary constants less than half that of untreated cotton, suggesting a very low tendency to be wetted. In fact, the capillary constant (K) has the following definition:¹⁷

$$K = 1/2 C \times r \times \varepsilon^2 (\pi R^2)^2 \quad (1)$$

where C is a tortuosity coefficient, r is the mean radius of the capillary tubes, ε is the porosity of the sample, and R is the mean hydrodynamic radius of the capillaries. Hence, the grafting treatment is able to reduce the wickability of cotton through significant modifications of the capillary network.

The results of water sorption tests are reported in Figure 1, in which the weight increase of small samples of fabric is recorded as a function of time during water wicking until equilibrium is reached. It is evident that untreated cotton absorbs at the same time much more water than the treated fabrics, followed by samples treated with Araldite DY-T and with CoatOSil 3503 emulsified with a 0.05 g/L surfactant solution. In the first case, the residual wettability could be due to the small amount of silicone additive, whereas in the other case, the emulsion could produce a polymer distribution not homogeneous enough. Thus, areas with low wettability alternate with others that can absorb as untreated cotton, yielding average unsatisfactory performances. The

TABLE VI
Results of UV Curing of Cotton Fabric with Araldite DY-T and BYK Additives After an Irradiation Time of 75 s on Each Side

Additive	Weight on Araldite (%)	Weight on cotton (%)	Gel content (%)	Yield (%)	Contact angle (°)
BYK 373	5.0	5.7	57.5	45.5	0
BYK 373	5.0	8.4	37.6	30.7	0
BYK 373	20.0	17.7	89.9	59.9	102
Silclean 3700	5.6	2.9	31.1	26.9	0
Silclean 3700	5.6	2.1	40.5	30.5	0
Silclean 3700	20.0	24.1	81.4	69.8	128

TABLE VII
Capillary Constant and Weight Increase Values at Equilibrium in Wettability Measurements of Various UV-Cured Cotton Fabrics

Sample	UV-cured resin	Diluent	Weight on cotton (%)	Capillary constant (cm ⁵)	Weight increase at equilibrium (g)
—	Untreated cotton	—	—	3.21×10^{-8}	0.114
01	CoatOSil 3503	Tergitol (0.05 g/L)	1.3	8.68×10^{-9}	0.028
02	CoatOSil 3503	Toluene	3.1	1.35×10^{-8}	0.008
03	CoatOSil 3503	None	23.8	4.94×10^{-9}	0.013
04	CoatOSil 3503	None	24.5	5.67×10^{-9}	0.008
05	CoatOSil 3503	Tergitol (1 g/L)	40.3	8.18×10^{-9}	0.004
06	CoatOSil 3509	Tergitol (1 g/L)	2.7	4.53×10^{-9}	0.034
07	CoatOSil 3509	None	22.5	1.16×10^{-8}	0.008
08	TEGO Rad 2600	None	20.1	1.63×10^{-8}	0.017
09	UCECOAT 7849	None	12.2	3.38×10^{-9}	0.001
10	AralditeDY-T (+5.6% Silclean)	None	2.1	1.20×10^{-8}	0.067
11	Araldite DY-T (+5.0% BYK 373)	None	5.7	9.29×10^{-9}	0.064

other materials showed poor weight increases, which indicated good water repellency. The values of the weight increase at equilibrium are compared in Table VII and show that the lower water adsorption was achieved with CoatOSil 3503, undiluted or diluted with toluene, undiluted CoatOSil 3509, and UCECOAT 7849.

Moisture adsorption and water vapor permeability

Some results of moisture adsorption at 93% relative humidity are compared in Table VIII. Cotton treated with silicone acrylate copolymers presents much lower values of adsorbed moisture than untreated cotton, even at low weight add-on, confirming the good water-repellent effect of the UV-curing treatment.

Tests of water vapor permeability were carried out to confirm differences between treated and untreated cotton in a humid atmosphere. Flasks were sealed with cotton UV-cured with CoatOSil and TEGO Rad

resins at different percentages after dilution with toluene to obtain a good distribution on the substrate. In the first series of tests, the whole system, composed of the flask, salt, cotton, and sealing, was weighed, and weight variations due to absorbed water vapor were referred to the initial salt weight (5 g), as reported in Figure 2. Flasks sealed with untreated cotton absorbed more water than the others, above all during the first 48 h and less for longer times. CoatOSil 3509 conferred more water repellency to cotton than CoatOSil 3503, whereas for both resins, there was a decrease in the absorption with an increasing weight percentage of the resin; this was more evident for the latter.

However, this test does not allow us to discriminate a weight increase due to water adsorbed on the cotton surface from that due to vapor passing through the fabric and absorbed by the salt. Therefore, more tests were carried out to confirm this aspect, in which for every resin and weighting percentage three flask systems were prepared and contemporarily put in a humid atmosphere. Once a day, only the salt inside one flask was weighed to evaluate the vapor amount absorbed by the salt that effectively crossed the fabric. In Table IX, the percentages of the weight increase of the salt are reported, show-

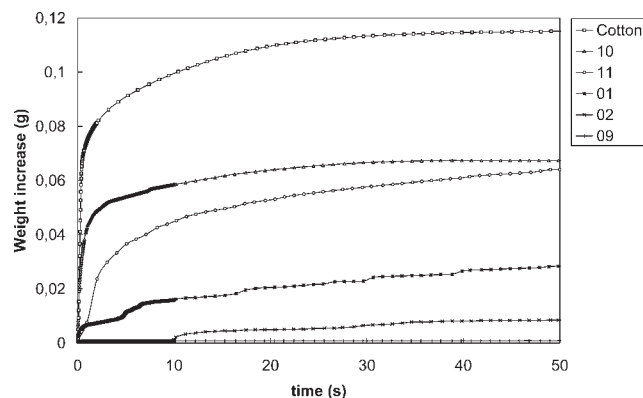


Figure 1 Wettability measurements with a Krüss 100 SF tensiometer. The sample numbers refer to Table VII.

TABLE VIII
Moisture Adsorption of Some Cotton Fabrics After 24 h of Exposure at 93% Relative Humidity

Resin	Weight on cotton (%)	Adsorbed water (%)
Untreated cotton	—	15.7
CoatOSil 3503	2.5	5.1
CoatOSil 3503	23.8	8.3
CoatOSil 3509	3.2	4.4
TEGO Rad 2600	2.6	3.5
TEGO Rad 2600	20.1	5.7

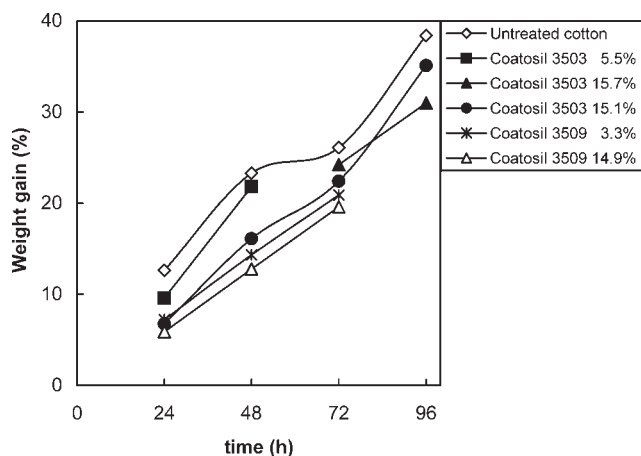


Figure 2 Water vapor permeability tests: weight gain of the measuring system with respect to the initial weight of the salt (5 g) versus the exposure time at 93% relative humidity (23°C).

ing poor differences between the various systems, although untreated cotton allowed less humidity to pass through, even if by a minimal amount. This means that the vapor permeability of cotton is not substantially affected by the treatment, and the weight differences recorded in the first test were due mainly to the water withheld by fabrics, whereas untreated cotton seems to withhold more moisture than treated samples.

TABLE IX
Water Vapor Permeability: Weight Increase of the Salt in Flasks Sealed with Various Cotton Fabrics After Exposure at 93% Relative Humidity

Test	UV-cured resin	Weight on cotton (%)	Weight increase of the salt (%)		
			24 h	48 h	72 h
A I	Untreated cotton	—	4.80		
A II	Untreated cotton	—		8.85	
A III	Untreated cotton	—			13.44
B I	CoatOSil 3509	4.0	4.85		
B II	CoatOSil 3509	2.7		9.79	
B III	CoatOSil 3509	3.6			13.64
C I	CoatOSil 3509	20.9	8.81		
C II	CoatOSil 3509	19.8		13.71	
C III	CoatOSil 3509	20.0			17.05
D I	CoatOSil 3503	3.7	6.45		
D II	CoatOSil 3503	4.4		9.54	
D III	CoatOSil 3503	3.7			15.23
E I	CoatOSil 3503	14.8	6.40		
E II	CoatOSil 3503	17.0		8.91	
E III	CoatOSil 3503	17.7			15.49
F I	TEGO Rad 2600	3.1	9.80		
F II	TEGO Rad 2600	2.5		10.28	
F III	TEGO Rad 2600	2.0			19.76
G I	TEGO Rad 2600	15.6	8.18		
G II	TEGO Rad 2600	16.3		9.25	
G III	TEGO Rad 2600	15.2			15.29

These results prove that the UV curing of cotton with silicone acrylates does not compromise the breathability of the fabric, confirming that only the surface properties of the fibers are modified. This aspect is very important for cloth comfort and differentiates the UV curing of cotton with these resins from a polymer coating obtained by the spreading of a mixture of oligomers followed by thermal cross-linking.

Morphology and surface analysis

SEM images of untreated cotton and cotton UV-cured with CoatOSil 3503 at a low polymer add-on are compared in Figure 3. In the treated fabric, the fibers mostly appear to be individually coated by a thin polymeric layer, and this confirms that the porosity of the fabric should be substantially unaffected. A similar morphology was shown by cotton UV-cured with the other resins.

EDX analyses showed the presence of Si on the surface of fabrics UV-cured with silicone resins. In Figure 4, the ratio of the peaks of Si and C is reported for samples UV-cured with various resins. TEGO Rad 2600 at 2.57% on cotton shows the highest value, whereas CoatOSil 3503 approaches the same value at a concentration 3 times higher. These

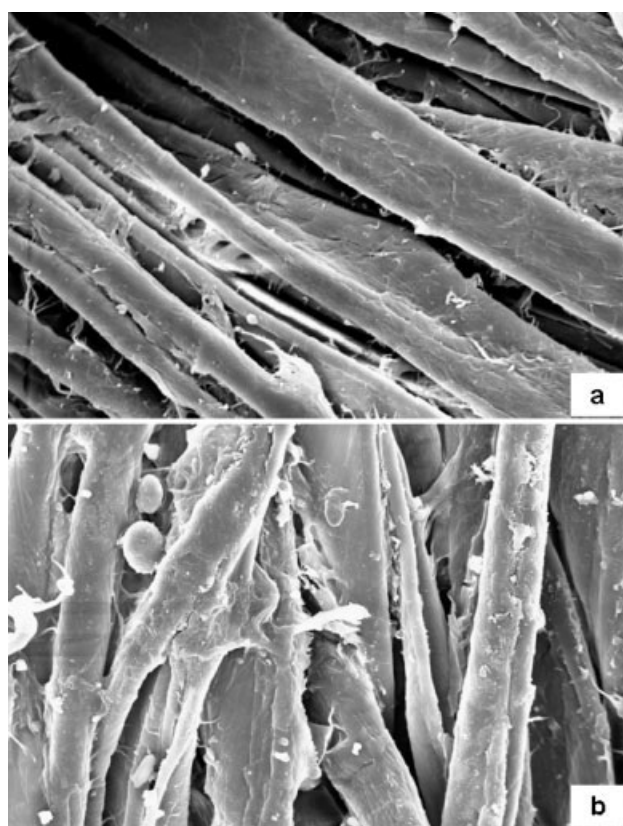


Figure 3 SEM images (1000×) of (a) untreated cotton and (b) cotton UV-cured with 2.5% CoatOSil 3503.

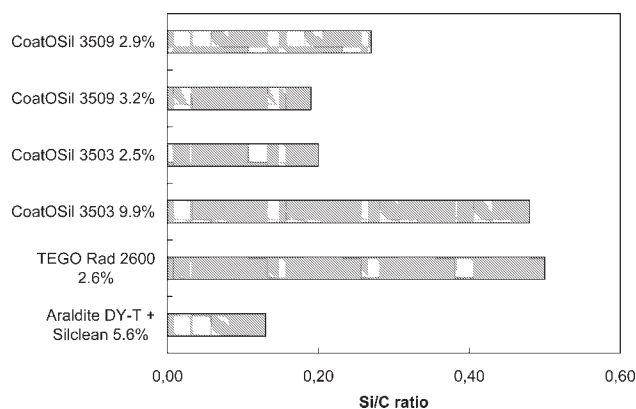


Figure 4 Comparison of the results of EDX analysis.

results agree with contact-angle measurements, which showed a higher water repellency effect of TEGO Rad 2600 at a low concentration.

CONCLUSIONS

Water-repellent cotton fabrics were prepared by UV-curing techniques, with the gel content and polymerization yield taken into account. Radical and cationic photopolymerizations were tested, but the best results of water repellency were found with radical UV curing of silicone or urethane acrylated resins, although cationic photopolymerization was able to confer a water-repellent effect when a typical epoxy resin was added with silicone hydroxyl-containing additives. The results for the contact angle, wettability, and moisture adsorption showed that water

repellency was significant already at a low resin add-on. Moreover, the treated fabrics maintained their own breathability, and SEM analysis confirmed that UV curing led to a coating layer on each fiber rather than a plain film on the fabric surface.

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