

Printing of reactive silicones for surface modification of textile material

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ABSTRACT: For outdoor sports, waterproof breathable materials are widely used to provide protection from environmental factors like rain and wind. The most important techniques to achieve excellent performance use perfluorinated organic substances, which must be replaced in the near future due to health concerns and their environmental persistency. Printing of textile materials with reactive silicone pastes could be an alternative to introduce water repellency without fluorocarbon finishing. In this work, production of barrier textiles through one-step silicon printing was studied, using a two-component paste with long pot life and a thermal fixation step. Three different knitted fabrics made from micromodal, polyamide/elastin, and cotton/polyester were used as substrates for the printing. The achieved hydrophobic modification of the fabric was analyzed by determination of water shedding angle, water resistance, water retention values, moisture content, air permeability, tensile properties, and infrared spectroscopy. The results indicate several areas of technical application for the modified fabric, such as barrier textiles with permeability control, localized modification of mechanical properties of fabric and garment. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42594.

KEYWORDS: biopolymers and renewable polymers; cross-linking; crystallization; mechanical properties; thermoplastics

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INTRODUCTION

In outdoor sports garment, waterproof breathable materials are used to provide protection from environmental factors like rain and wind. Methods to achieve performance on apparel include yarn modification, e.g., usage of fiber blends, optimized construction of textile fabric including finishing operations, e.g., coating, printing, and use of multilayered fabrics, e.g., laminates.^{1,2} High water resistance and permeability for water vapor can be achieved by use of membrane textiles, however, the presence of a waterproof membrane limits the permeability of the fabric for water vapor.³ Moisture transport through materials has been studied extensively and represents an important parameter determining the comfort properties.^{4,5}

High-performance water repellent finishes still base on fluorocarbon (FC)-containing products, however, these materials are under severe criticism due to their content of hazardous by-products, e.g., perfluorooctane carbonic acid in C-8 fluorocarbon products and their persistence in the environment of both C-8 and C-6 fluorocarbon products.^{6,7} As a result, intensive research is ongoing to

develop methods which will allow replacement of the very powerful FC products in water-repellent textile applications, by more environmentally friendly products, e.g., based on hydrocarbons, fatty acid derivatives, dendrimer products, or silicones.^{8,9}

Silicone compounds offer a wide range of possible chemical modification with regard to molecule size and reactive groups present.^{10,11} By combination of different vinyl group containing siloxanes, reactive silicone formulations can be prepared, which cross-link at elevated temperature in the presence of a Pt catalyst. An example for the basic chemical structure is given in the Supporting Information (Figure S1). After printing at room temperature, during curing, physical, and chemical bonds are created between the silicone macromolecules and the material reaches its definitive state.^{12,13} Such formulations also could be applied in printing techniques.¹⁴ Printing of silicone oligomers and polymers already has been studied for different technical applications, e.g., liquid crystal displays.^{15,16}

Silicone coating of textile fabrics allows the modification of physical properties of technical fabrics, which has been

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Table I. Physical Properties of the Base Fabric Used and Add-on of Printing Pastes (\pm Standard Deviation)

Sample		Composition (% w/w)	m/A (g/m ²)	Add-on with Si paste 1 (%)		Add-on with Si paste 2 (%)	
MIM	Mikro modal	100	107	137	± 25	103	± 29
PAEL	Polyamid/Elastin	60/40	230	82	± 17	53	± 9
CoPES	Cotton/Polyester	60/40	179	91	± 15	47	± 4

reported in the literature.^{17–20} As an example in technical textiles, tensile properties of fabrics were modified by printing of silicone pastes.^{21–24} The major part of silicone polymers applied at present in textile processing bases on reactive silicone polymers which cross-link in presence of moisture. This technique is rather simple to use, however, control of reactivity in the applied silicon is difficult. Pt-catalyst-based two-component silicon pastes have already reached the market for color printing on a wide range of textile substrates. Through its favorable mechanical properties, printing of reactive silicone polymers could open a new production strategy to obtain textile materials with barrier function for application in outdoor clothing.^{1,2} Instead of laminating a microporous membrane in combination with a water-repellent finish, the formation of the hydrophobic barrier then could be achieved by one screen printing step. Thus, application of reactive silicone polymers in screen printing could open a route for a more ecological production of barrier textiles. As the amounts of expensive Pt catalyst required in the paste are at the level of few ppm, the process will also be economically viable, compared to membrane laminates or fluorocarbon finishes.

The aim of this work is to examine modifications that can be achieved on different knitted fabrics by printing reactive silicone materials, with regard to future application for functional textiles, e.g., sports apparel. Modification of physical properties of three different textile materials made from micromodal, polyamide/elastin, and cotton/polyester, which served as substrates for printing of reactive silicone pastes, was investigated in this study. Samples were characterized by optical microscopy, Fourier transform infrared spectroscopy (FTIR), and by determination of technical properties such as water retention values, moisture content, water shedding angle, water repellency, air permeability, and tensile properties.

EXPERIMENTAL

Materials

Materials used in these experiments were all knitted fabric: micromodal (MIM, 107 g/m², Lenzing AG, Lenzing, Austria), polyamide-elastin (PAEL, 60% PA, 40% EL w/w, 230 g/m², Feinjersey, Götzis, Austria), and cotton-polyester (CoPES, 179 g/m², Fussenegger Textil, Dornbirn, Austria). Details of the materials are given in Table I.

MIM was supplied in prewashed state, CoPES was supplied in scoured and bleached state. PAEL was washed before printing to remove oil and preparation from fabric production. A sample with 520.45 g mass was treated in 2500 mL water (60°C, 30 min) in presence of a nonionic surfactant (0.75 g/L Marlipal 013/69, Sasol, Marl, Germany) and Na-polyphosphate (0.75 g/L, Calgon). Then the material was rinsed twice in water at room temperature for 5 min and dried in air for 24 h.

Silicone Printing

Components for silicone pastes used in this study were delivered by CHT Austria R. Beitlich GmbH Company (Meiningen, Austria). Platinum(0)–1,3-divinyl-1,1,3,3-tetramethyl-disiloxane complex solution was used as delivered (Sigma, Aldrich, CAS number: 68478-92-2).

The preparation of the silicone mixtures as printing pastes was as following: first 5 g vinyl modified polysiloxane (SFA 42200), 15 g vinyl modified polysiloxanes (SFA 42102 or SFA 42103), and 5 g H-siloxane/dimethyl siloxane copolymer (SFA 11230) were mixed in a plastic beaker and stirred for 15 min. In another plastic cup, 0.025 g Pt catalyst and 0.025 g vinyl modified poly siloxanes (SFA 44012), which acts as an effective retarder, were mixed and then the mixture from the first plastic cup was added and the paste was mixed for 15 min. Details of the silicones used are given in Table II. In water-based printing processes, the viscosity of the paste can be adjusted by the

Table II. Physical and Chemical Characteristics of the Silicone Materials Used to Prepare Silicone Pastes 1 and 2 and Composition of the Pastes

Silicon	Modification	Viscosity (mPa s)	Vinyl content (mmol/g)	SiH content (mmol/g)	Density (g/cm ³)	Paste 1 (g)	Paste 2 (g)
SFA 42200	End modified	200	0.25		0.97	5	5
SFA 42102	End modified	1000	0.13		0.97	15	0
SFA 42103	End modified	10000	0.05		0.97	0	15
SFA 44012	Cyclic	100	1.18		1.02	0.025	0.025
SFA 11230	Side modified	210		2.3	0.97	5	5
Pt catalyst						0.025	0.025

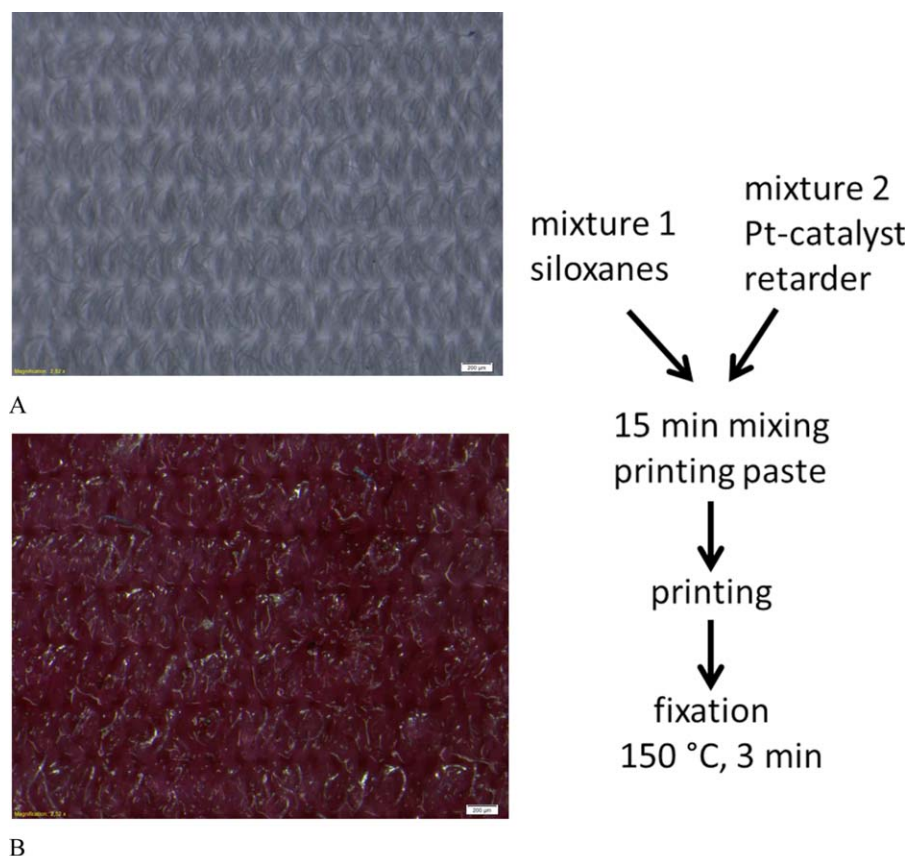


Figure 1. General scheme of paste preparation and printing, and representative examples for the effect of silicone printing. (A) PAEL reference fabric; (B) PAEL with silicone paste 2 (marked red for better visibility, Scale bar 200 μm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

amount and type of thickener used; in the case of the siloxanes used, the printing paste does not contain any thickener system to modify viscosity. Thus, the viscosity of the paste was adjusted by mixing siloxanes with different viscosity.

Flat screen printing was performed using a 15×15 cm printing area and a plain weave screen fabric (SEFAR 90/230-40, 90 mesh/cm, thread diameter 40 μm , 37% open area, Heiden, Switzerland). Fabric samples were fixed on a plane table by adhesive tape and the printing screen was placed on the fabric. The silicone was filled on the closed part of the screen and printed through the open area by means of a squeegee. Five samples were prepared for each fabric type. After printing at room temperature, the prints were cured at 150°C for a period of 3 min to initiate the cross-linking reaction (Figure 1). The add-on given in Table I was calculated from the increase in mass in the printed area, according to eq. (1).

$$\text{Add} = 100 \times (m_p - m_a) / m_a \quad (1)$$

With m_a and m_p being the sample mass in grams before and after printing, respectively.

Characterization Techniques

The ATR-FTIR spectra were recorded with a Vector 22 spectrophotometer (Bruker, Germany), equipped with a diamond ATR

unit. Spectra were registered in the wavenumber interval from 4000 to 400 cm^{-1} with 32 scans and a resolution of 4 cm^{-1} .

For determination of the water shedding angle (WSA), stainless-steel needles were used to produce water drops with defined volume. A tube pump was used to generate drops of a volume of 5.0 ± 0.3 μL (Ismatec MV GE, Ismatec, Glattbrugg, Switzerland). For determination of WSA, water drops were released onto the samples starting at an inclination angle of 85°. Five different positions were tested. The inclination angle was reduced in steps of 5° up to the angle where one or more of the drops did not roll off the sample completely. The given WSA represents the lowest inclination angle at which all drops rolled off the surface of the test specimen. The distance between release of drop and sample surface was (10.0 ± 0.5) mm. Three repetitions were made for each sample. All experiments were performed at ambient conditions.^{25,26}

The air permeability was performed using a Textest instrument FX3030 (TEXTTEST, Austria), according to International Standard BS EN ISO 9237:1995 - Textiles-Determination of the permeability of the fabric to air. The tests were performed in the standard atmosphere. A test surface area of 20 cm^2 and a pressure drop of 100 Pa were used as recommended for apparel fabrics.²⁷ Air permeability, R , expressed in millimeters per second (mm/s), was calculated according to eq. (1).

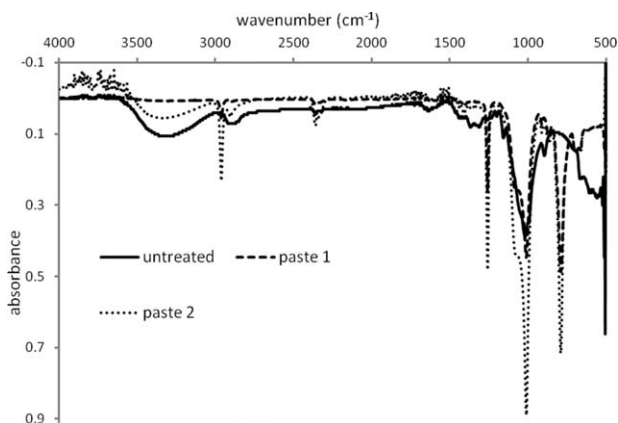


Figure 2. ATR spectra for MIM fabric untreated, and printed with paste 1 or paste 2.

$$R = \frac{q_v}{A} \cdot 167 \quad (1)$$

Where q_v is the flow rate of air, dm^3/min ; A is the area of fabric under test, cm^2 ; and 167 is the conversion factor from dm^3/min to mm/s .

The water resistance was performed using a Textest instrument (TEXTTEST FX 300 Hydrotester III, Switzerland), according to AATCC Test Method 127-2003. Water Resistance: Hydrostatic Pressure Test, AATCC Technical Manual, 2008. Specimens were conditioned before the test at $21 \pm 2^\circ\text{C}$ at $65 \pm 2\%$ RH for at least 4 h. The samples were tested with the printed side directed toward the water. In this test, fabric samples were fixed in ring clamp with 114 mm open diameter and distilled water was brought in direct contact to the surface. The hydrostatic pressure of the water then was increased by a rate of 10 mm of hydrostatic head per second until water penetrates the specimen. The pressure for water breakage for the first and third drop was recorded and the mean of three repetitions was calculated.²⁸

For determination of the water retention volume (WRV) and the moisture content (MC), samples were weighed (m_3) after acclimatization for 24 h in normal climate ($21 \pm 2^\circ\text{C}$, $65 \pm 2\%$ RH). A mass of 0.5 g of fabric/fibers was placed in 50 mL of distilled water in a glass bottle and kept at room temperature for 24 h. The samples were removed from the glass bottles into a plastic centrifuge tube where capillary water was removed by centrifugation (Multifuge 1L, D-37520 Osterode, Germany). After centrifugation at 5578 rpm for 10 min ($4000 \times g$), the weight of the wet samples was determined (m_1). The samples were dried at 105°C for 4 h and after cooling down in the desiccator over (P_2O_7) for 24 h, the weight of the dry samples was determined (m_2). Value of WRV was calculated according to Eq. (2).²⁹

$$\text{WRV} = \frac{m_1 - m_2}{m_2} \cdot 100 \quad (2)$$

where m_1 and m_2 are the wet mass (g) and mass after drying (g), respectively. Three independent measurements were performed and values are given as mean and standard deviation.²⁹

MC was determined according to Eq. (3).

$$\text{MC} = \frac{(m_3 - m_2)}{m_2} \cdot 100 \quad (3)$$

With MC as moisture content in %, m_3 as mass of conditioned fabric (g), and m_2 as mass of dry fabric (g).

A universal testing machine (Zwick/Roell Z010, Germany) was used to determine the tensile force as function of elongation applied according to the recommendations of DIN 53835. Each set consisted of at least three test specimens in the whale direction. The width of each test specimen was 20 ± 0.5 mm and its length was 50 ± 0.5 mm. Samples were tested for cyclic loading to max. elongation of $\pm 20\%$. Two load-extension cycles were performed. After completing the first cycle and a recovery time of 60 s, the second cycle was repeated under the same conditions.

RESULTS AND DISCUSSION

Silicon Printing

Flat screen printing was performed using a printing frame with open area of 15×15 cm. Two silicone pastes 1 and 2 were used for coating. The reaction rate of the Pt-catalyzed hydrosilylation depends on the amount of catalyst added. In screening experiments, the amount of Pt-catalyst in the printing pastes was reduced to such a level that thickening and cross-linking at room temperature could be retarded for approximately 4 h, which thus allowed application of the mixture in screen printing. Cross-linking reaction then was initiated by a temperature increase to 130°C .

The amount of paste printed on the fabric was determined by the mesh size of the printing screen and the viscosity of the paste. The mass of paste printed per m^2 was approximately $166 \text{ g}/\text{m}^2$ for paste 1 and $105 \text{ g}/\text{m}^2$ for paste 2. Depending on the mass per area of the fabric, the calculated add-on in percentage of fabric weight was different (Table I).

With silicone paste 1, lowest add-on was observed for PAEL with 82%, and 91% were calculated for CoPES and highest value was found for MIM with 137%. Lower values were determined for the higher viscous paste 2 with 47% for CoPES, 53% for PAEL, and 103% for MIM.

Microphotographs of representative samples are shown in Figure 1. For better visibility, a red dye was added to the silicone paste.

FTIR Analysis

FTIR-ATR spectra for MIM, PAEL, and CoPES fabric and printed fabric with silicone paste 1 and 2 are given in Figure 2, and Supporting Information, Figures S2 and S3, respectively. The silicone printing is expected to modify the fabric surface. Thus, ATR spectra were recorded as this method allows monitoring of substances located more near to the fabric surface. Formation of silicone products, for example, Si—C, Si—O—Si, and Si— CH_3 groups will be indicated by their characteristic absorbance in the wavenumber interval $798\text{--}1261 \text{ cm}^{-1}$.³⁰

FTIR-ATR analysis for MIM fabric and printed samples with silicone paste 1 and paste 2 exhibited the characteristic absorbance peaks for cellulose II, represented by peaks of the intramolecular

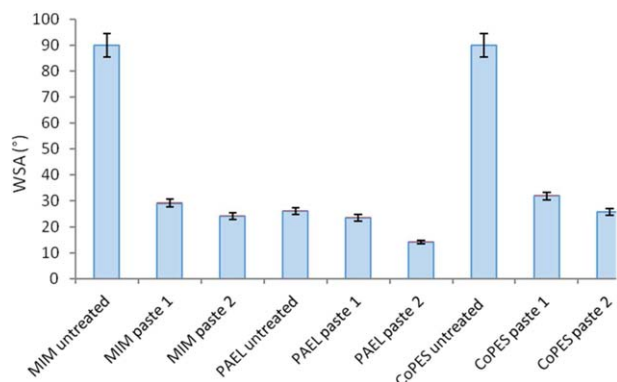


Figure 3. Water shedding angle for untreated and treated fabric. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrogen OH•O bond in the range $3455\text{--}3410\text{ cm}^{-1}$ and C—H stretch in the range $3000\text{--}2800\text{ cm}^{-1}$. Characteristic absorptions for cellulose II were observed in the range $1300\text{--}1000\text{ cm}^{-1}$ (C—H, C—O vibration). Formation of silicone products was detected by the characteristic absorbances as described above. FTIR-ATR spectra for PAEL fabric and prints with silicone paste 1 and 2 are given in Supporting Information, Figure S2.

Characteristic absorbances for PA and elastin were recorded around 3300 cm^{-1} (N—H bond), 2928 cm^{-1} (C—H), and in the range $1639\text{--}1531\text{ cm}^{-1}$ (O=C—N and N—H amide I and II vibration). Presence of silicone products was demonstrated by the characteristic absorbances for Si—C, Si—O—Si and Si—CH₃ bondings. ATR spectra for CoPES fabric and prints with silicone pastes 1 and 2 are given in Supporting Information, Figure S3. FTIR-ATR analysis for CoPES fabric and prints with silicone paste 1 and paste 2 exhibited the characteristic peaks for polyester and cellulose (O—H stretching 3350 cm^{-1} , C—H stretching 2900 cm^{-1} , C=O stretching 1720 cm^{-1} , CH₂ 1429 cm^{-1} , C—O stretching 1058 cm^{-1}) and silicone.

Water Repellency

The hydrophobic properties were characterized by determination of the WSA for the dynamic wetting property and the water resistance for the static wetting property.²⁵ The WSA characterizes the resistance of a fabric surface against the impact of a falling drop, while the water resistance describes the tightness of the fabric in direct contact to a water surface under increasing hydrostatic pressure. Certain properties of a material will be emphasized in a chosen test method dependent on the physical principles behind test protocol applied. Thus, a discussion of hydrophilic or hydrophobic properties always has to consider the general behavior of a material under the conditions of the test environment. Figure 3 summarizes the results of the water shedding angle measurements for untreated and treated fabrics. Highest reduction in WSA was observed when hydrophilic cellulose material was modified with silicone.

The different water repellency of the printed materials could be highlighted by the water shedding angle measurements. For untreated MIM fabric, shedding angle was $>85^\circ$ because the

material fabrics are too hydrophilic and for MIM treated with silicone paste 2, WSA was about 24° . For untreated PAEL fabric, WSA was about 26° which changed to 11° after printing with paste 2. The rather low WSA angles in case of untreated PAEL can be explained with the dense knitted structure of the PAEL fabric and the compact fabric surface, which supported roll-off of the water drop even at comparable low WSA angle. For untreated CoPES fabric shedding angle was $>85^\circ$ because the fabric was very hydrophilic, which reduced to 25° with silicone paste 2.

In unmodified state, all three different fabrics showed hydrophilic behavior, thus measurement of water resistance was possible only for the silicone printed samples. Values for water resistance after modification with silicone pastes 1 and 2 are shown in Figure 4. Highest values up to 260–304 mm were achieved on PAEL using silicone paste 2. In case of paste 2, approximately 121 g of silicone were printed per m² while for paste 1 (as a result of the lower viscosity) values near 188 g/m² were applied. Despite the lower amount of paste printed per m², printing with silicone paste 2 led to higher water resistance compared to the results with paste 1. This can be explained with the higher viscosity of paste 2 which helped to form a dense layer near to the surface (Figure 1).

Under the dynamic test conditions of the WSA test, mainly the surface properties of the fabric will determine the results. On a plane smooth surface, the small water drops will roll off easily and contact time for wicking into a fabric structure is low. In the case of the water resistance test, the contact time between the static water surface and the fabric is within several minutes. Thus wicking into the fabric structure is possible. Hydrophobicity of the fabric and technological parameters of the fabric such as wettability, fiber material, or porosity become determining factors. The rather hydrophilic PAEL showed low values in the WSA test, while in their untreated state, none of the three tested fabrics could be tested for water resistance. The formation of a hydrophobic barrier through silicon printing increased the barrier function to a level which allowed testing of the water resistance.

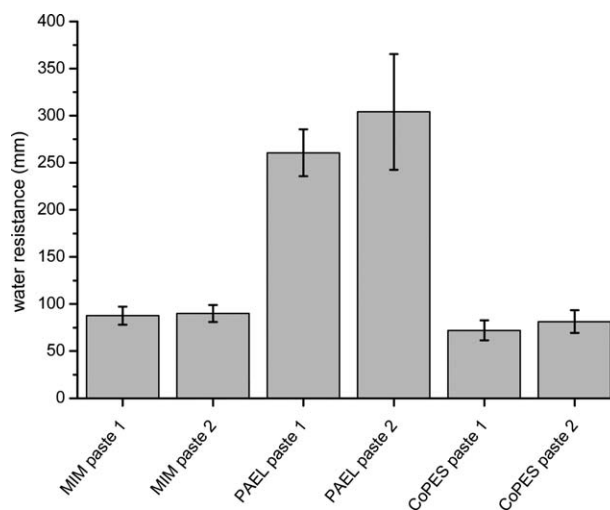


Figure 4. Water resistance for silicone-modified fibers paste 1 and 2.

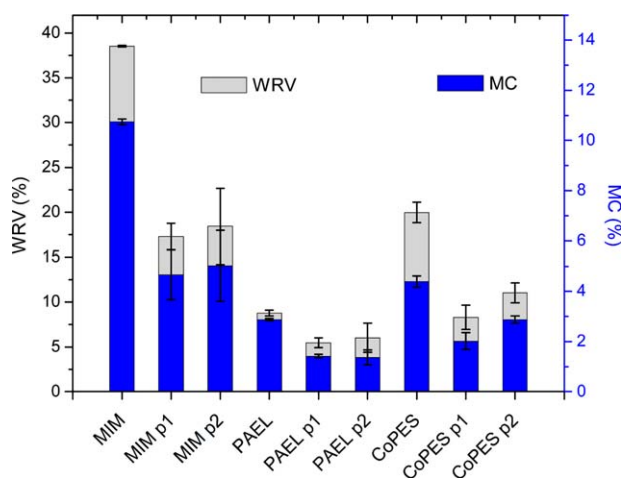


Figure 5. Water retention values (WRV) and moisture content of untreated and modified fabric. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Microphotographs of both sides of the different printed fabrics are shown in Supporting Information (Figures S4–S6). Through printing of the silicon paste, a coating of the knitted yarn structure in the fabric could be achieved. Dependent on the loop density of the fabric, an impermeable silicone barrier is formed. In case of MIM and CoPES, the film-forming properties of paste 2 still are not sufficient to develop a fully covering silicone barrier. Large pores are observed between the yarn loops in the fabric. In case of the more dense fabric structure of PAEL, a dense silicone barrier is formed. This tight barrier explains the relatively high values observed in the water resistance test.

The formation of a more closed material structure should be accompanied by a reduction in air permeability. Air permeability, R , expressed in millimeters per second (mm/s) for MIM, PAEL, and CoPES are given in Supporting Information, Figure S7. Air permeability of untreated fabrics ranged from 100 mm/s for PAEL to 8400 mm/s for MIM. Air permeability of the treated fabrics were significantly lower compared, with the lowest value of 6.09 mm/s for PAEL printed with silicone paste 2.

All three fabrics MIM, PAEL, and CoPES exhibited significant water uptake due to swelling and capillary water. Water which is held in the fabric structure in capillary spaces can be removed by centrifugation. Thus, a decrease in WRV indicates the filling of capillary spaces and fiber coating by the silicone polymer. The results of WRV determination before and after silicone treatment are shown in Figure 5.

WRV of untreated fabrics ranged from 19.9 to 38.5% w/w and was significantly lowered by the application of the silicone pastes. Lowest WRV was determined for PAEL fabric after treatment with paste 1, where values of 3.5% w/w were obtained. The lower viscosity of paste 1 led to a deeper penetration of the silicone print into the fabric structure; thus, as a general tendency, paste 1 exhibited more distinct reduction in WRV.

Moisture content (MC) for MIM, PAEL, and CoPES before and after printing with silicone paste 1 and 2 are given in Figure 5.

MC of untreated fabrics ranged from 4.4 to 10.7% w/w. MC of the treated fabrics were significantly lower, highest decrease to MC of 1.4% w/w was determined for PAEL applying silicone paste 2. Similar to that in the WRV determination, the additional mass of a hydrophobic component reduces the determined overall moisture content calculated in % w/w. Thus, the major part of the observed effect, however, is due to the presence of hydrophobic silicone polymer in the fabric structure.

The micromodal fiber used in MIM exhibits high swelling in water, leading to a WRV of nearly 40% for the untreated fabric. After silicon printing, the experimentally determined value for WRV reduces to 17–18%. This reduction is caused by the presence of non-swelling hydrophobic silicone which now represents approximately 50% of the mass of fabric. The reduction of the WRV thus is not due to a chemical modification of the cellulose fibers as the WRV of the silicone treated sample is very similar to the expected value of a fiber blend containing 50% of micromodal and 50% of a hydrophobic fiber. The results of CoPES and PAEL exhibit the same behavior, thus silicon printing primarily leads to formation of a hydrophobic coating layer, chemical modification of the textile fibers is of minor relevance.

The tensile force–elongation curves were recorded under cyclic loading to a sample elongation of 20%. Two load extension cycles were performed with a recovery time of 60 s between the two cycles. Load-extension cycles for cycles 1 and 2 of untreated fabrics and printed samples are given in Figure 6 for CoPES and as Supporting Information, Figure S8 for MIM and Figure S9 for PAEL. In all cases, a significant modification of the force elongation properties could be achieved by the silicone printing. Through formation of an elastic silicone polymer layer in the fabric structure, a higher tensile force was required to stretch the samples by 20%. Despite the lower amount of silicone polymer in the fabric, the higher tensile force was observed for

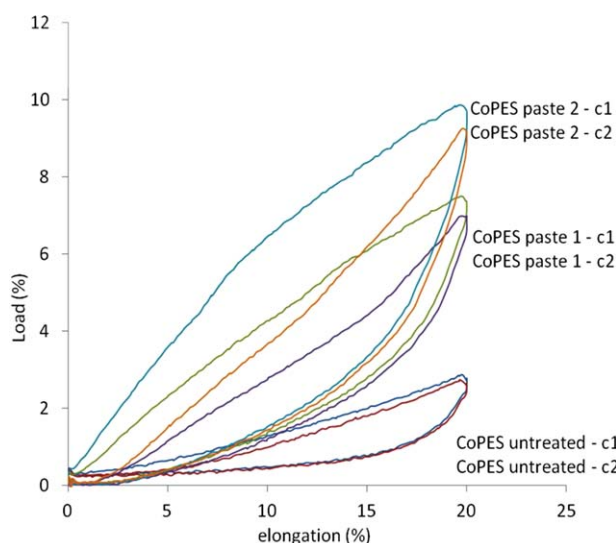


Figure 6. Force–elongation curves of untreated CoPES fabric and modified samples (c1 = first load extension cycle, c2 = second load extension cycle). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

samples printed with paste 2. Elasticity was not reduced negatively by the silicone polymer, which is indicated by the small hysteresis between load and release cycles.

The insertion of an elastic silicone into the porous fabric structure also led to substantial changes in tensile force–elongation behavior. The tensile force required to achieve an elongation of 20% almost doubled, while elasticity remained at the same high level.

CONCLUSIONS

Through appropriate adjustment of pot-life, silicone barrier textiles can be produced in a printing process. During screen printing at room temperature, the hydrophobic silicone barrier remains in viscous state and can be positioned near the surface of the textile. In the following thermal cross-linking step, the final polymer structure forms and a hydrophobic barrier near the surface of the product results. During the thermal curing also, the viscosity of the print decreased which led to a rather high penetration of the reactive silicone into the textile structure. The silicone polymer print permits modification of water-related properties as well as mechanical properties.

The water and air permeability of the treated fabric can be adjusted by appropriate selection of fiber material, fabric structure, and printing conditions, e.g., dense layers will result from a combination of fabric with high loop density and viscous printing pastes, while a more porous open structure will be obtained on a fabric with low loop density.

All materials tested showed a reduction in water binding capacity, as indicated both by reduced moisture sorption and lowered water retention values. The results indicate that the major principle of the process is based on the formation of a cross-linked silicone polymer structure inside the fabric rather than a chemical modification of the fiber.

Application of silicone printing can be of interest for a number of technical textile applications:

- barrier formation though full coverage printing for permeability control in textile garment;
- replacement of fluorocarbon-based water repellent finishes by silicone-based prints;
- localized printing for modification of stress-extensibility behavior in technical textiles;
- pigment colored printing permits combination of functional effects with pattern formation.

At present, the technology is applicable in screen printing; however, dependent on the technical requirements of the printing system, e.g., viscosity, also digital printing techniques will be applicable. Further investigations should address modification of the process to hold the silicone print more near the fabric surface. This would help lowering the required amount of silicone polymer to achieve a certain effect and to increase the overall performance more near the level of present fluorocarbon based finishing. Also the behavior of the silicon printing under prolonged mechanical stress–relaxation as well as

possible ageing during laundry processes will be of future interest.

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REFERENCES

1. Shishoo, R. *Textiles in sport*; Woodhead Publishing Limited in association with The Textile Institute. Press: New York, ISBN 10 1 85573 922 4, **2007**, 364 pp.
2. Laing, R. M.; MacRae, B. A.; Wilson, B. A.; Wilson, Ch. A.; Niven, B. E. *Text. Res. J.* **2011**, *81*(17), 1828.
3. Stockton, W. J.; Warw, W. U.S. Patent 7,842,625, **2010**, 1.
4. Adler, M. M.; Walsh, W. K. *Text. Res. J.* **1984**, *54*(5), 334.
5. Das, B.; Das, A.; Kothari, V.; Fanguiero, R.; Araujo, M. D. *J. Eng. Fibers Fabrics* **2009**, *4*(4), 20.
6. Lasier, P. J.; Washington, J. W.; Hassan, S. M.; Jenkins, T. M. *Environ. Toxicol. Chem.* **2011**, *30*, 2194.
7. Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Sulbaek Andersen, M. P.; Wallington, T. J. *Environ. Sci. Technol.* **2004**, *38*, 3316.
8. Roshan, P. *Functional Finishes for Textiles: Improving Comfort, Performance and Protection*; Woodhead Publishers: Cambridge, UK, ISBN 9780857098399, **2015**, p 407.
9. Harris, H. B. New York; **2013**, pp 229.
10. Jiang, B.; Huang, Y. D.; Wang, Q. *Mater. Res. Exp.* **2014**, *1*(2), 25.
11. Lee, J. K.; Char, K.; Rhoc, H. W. *Polymer* **2001**, *42*(21), 9085.
12. Lewis, L. N.; Stein, J.; Gao, Y.; Colborn, R.; Hutchins, G. *Plat. Metals Rev.* **1997**, *41*, 66.
13. Marciniak, B. *Comprehensive Handbook on Hydrosilylation*; Pergamon Press: Michigan, **1992**.
14. de Gans, B. J.; Duineveld, P. C.; Schubert, U. S. *Adv Mater.* **2004**, *16*, 203.
15. Chae, S. S.; Min, H.; Lee, J. H. *Adv Mater.* **2013**, *25*, 1408.
16. Jiang, B.; Mostofizadeh, A.; Bai, Y. P.; Huang, Y. D. *J. Phys. Chem. B* **2011**, *115*, 14526.
17. Iwata, M.; Harada, Y. U.S. Patent 2007/0100065 2007, 03.05.2007, 1.
18. Chen, Y. U.S. Patent 2012/0251798, 2012, 04.10.2012, 1.
19. Yu-Ping, L. U.; Tyler, W. U.S. Patent 2010/0268144 2010, 21.10.2010, 1.
20. Zhan, Z.; Chen, Y.; Wang, J. *Adv Mater. Res.* **2011**, *287–290*, 2644.
21. Caldas, V.; Brown, G. R.; Nohr, R. S.; MacDonald, L. E. *Enhancement of IPP Properties* **1997**, *65/9*, 1759.

22. Gulbinieneė, A.; Jankauskaitė, V.; Kondratas, A. *Fibres Textiles East. Eur.* **2011**, *19*(3), 78.
23. Bulut, Y.; Sular, V. *Mater. Manufact. Processes* **2013**, *28*, 106.
24. Budden, G. D.; Kosal, M. D.; Rolley, P. A. U.S. Patent 6,354,620 2002, 12.03.2002, 1.
25. Zimmermann, J.; Seeger, S.; Felix, A. R. *Text. Res. J.* **2010**, *79*(17), 1565.
26. Ramachandran, T. *IE (I) Journal-TX* **2004**, *84*, 37.
27. BS EN ISO 9237:1995. Textiles-Determination of the permeability of the fabric to air The British Standard, 2002.
28. AATCC Test Method 127-2003. Water Resistance: Hydrostatic Pressure Test, AATCC Technical Manual, 2008.
29. Bechtold, T.; Groner, S.; Ehrhardt, A. *Fibres Textiles East. Eur.* **2007**, *15*, 64.
30. Smith, A. L. *Spectrochim. Acta* **1960**, *16*, 87.