

Fabrication of superhydrophobic cotton fabrics by a simple chemical modification

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Abstract Hydrophobization of cotton fabrics was carried out with the use of bifunctional polysiloxanes with various contents of functional groups. Polysiloxanes contained in their structure groups capable of bonding to substrates (trialkoxysilyl or glycidyl ones) and fluoroalkyl groups showing surface activity. Two methods of surface modification were compared: (1) a one-step method via the chemical modification of fabrics with solutions of bifunctional polysiloxanes and (2) a two-step method—via preliminary modification of fabrics with silica sol followed by chemical modification with solutions of bifunctional polysiloxanes. The hydrophobicity was determined by measuring the water contact angle by drop profile tensiometry. Changes in the surface topography were examined by scanning electron microscopy. Superhydrophobic fabrics were obtained by a simple one-step method by the chemical modification in solutions of bifunctional polysiloxanes. The fabrics maintained

their superhydrophobic properties even after multiple washings. The modification does not cause any changes visible to the naked eye, such as stiffening, color changes or a decrease in mechanical properties.

Keywords Superhydrophobicity · Cotton fabrics · Polysiloxane · Sol–gel · Dip coating

Introduction

In recent years, there has been increased interest in the research and production of highly hydrophobic natural textiles due their unique characteristics such as self-cleaning, anti-contamination and anti-sticking (Ivanova and Zaretskaya 2011; Erasmus and Barkhuysen 2009; Xu et al. 2011). Natural fibers consists mainly of cellulose, hemicelluloses, lignins and pectins, the structures of which contain, among others, hydroxyl groups. In spite of the many advantages of natural fibers, they cannot be applied for many purposes because of their high polarity and hydrophilicity (resulting mainly from the presence of hydroxyl groups). The excessive moisture absorbability weakens materials made from natural fibers (a decreased adhesion), and at the same time it favors the growth of microorganisms (fungi, molds, bacteria). To bypass the above disadvantages, natural fibers are subjected to specific modifications of their surfaces aimed at creating an appropriate hydrophobic barrier. Non-

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wettable textiles with a high water contact angle (WCA), particularly the superhydrophobic ones (i.e., those with $\text{WCA} > 150^\circ$), are a contemporary research topic because of the significant commercial and industrial importance of low-surface-free-energy cellulosic materials for different apparel and technical applications such as protective clothing, stain-resistant fabrics and clothing for medical personnel. The wettability of a surface depends on two factors: (1) its chemical composition and (2) its structure (roughness). Different techniques for producing rough surfaces were developed by imitating nature (biomimetics); however, in textile production most of them cannot be recreated. Only the introduction of nanotechnology processes, such as electrospinning (Hutmacher and Dalton 2011), plasma treatment (Kan et al. 2011; Mihailović et al. 2011; Patiño et al. 2011; Sun and Qiu 2012; Vasiljević et al. 2013) and sol–gel technology (Mahltig 2011; Bae et al. 2009; Vilčnik et al. 2009; Zhu et al. 2011; Zhao et al. 2010; Simončič et al. 2012; Shateri-Khalilabad and Yazdanshenas 2013; Berendjchi et al. 2011; Chen et al. 2010), have enabled breakthroughs in the creation of superhydrophobic and self-cleaning textiles. In particular, the latter are very popular because the production and application of particles and nanoparticles on a surface make it possible to easily control its roughness. The mild preparation conditions offer the possibility of incorporating a wide range of labile organic species. Moreover, sol–gel-derived materials exhibit tunable porosity, transparency, hardness and good thermal stability (Basu et al. 2010; Xu et al. 2010). There are several kinds of inorganic nanosize particles, such as SiO_2 , TiO_2 and ZnO , which can be introduced onto the textile surface. However, this method only enables producing a suitable roughness of the surface, whereas to make it strongly hydrophobic, a chemical modification is necessary. Sometimes in the sol–gel process compounds such as, e.g., alkyltrialkoxysilanes (Mahltig and Böttcher 2003; Xu et al. 2011; Shateri-Khalilabad and Yazdanshenas 2013; Pipatchanchai and Srikulkit 2007) or functionalized silicas (Leng et al. 2009; Xue et al. 2009; Zhang and Wang 2013; Hoefnagels et al. 2007) are directly employed, which form a layer of a desired roughness and low surface energy during the condensation with tetraethoxysilane. Another possibility consists of the chemical modification of fibers with an earlier created roughness using various compounds in both the dip-coating

and vapor phase deposition methods (Zhou et al. 2013). Among the most effective hydrophobizing agents are fluorine-containing compounds (McKee 2006). In particular, the best effect is obtained by applying fluoro derivatives of organosilicon compounds, which combine unique properties of both components (Owen and Dvornic 2012). Among this group of compounds, the most frequently applied ones were fluorofunctional trichloro- and trialkoxysilanes (Leng et al. 2009; Pipatchanchai and Srikulkit 2007; Textor and Mahltig 2010; Hayn et al. 2011) as well as fluorosilyl amide (Evsyukova et al. 2009, 2011; Ivanova and Zaretskaya 2011). On the other hand, classical polysiloxanes were used relatively rarely because of difficulties with their adhesiveness and durability of bonding to fibers. For this reason, organofunctional polysiloxanes with hydroxyl, epoxy or amino groups in their structure have found the application to practice (Mahltig and Böttcher 2003; Vince et al. 2006) because the above groups are capable of reacting with functional groups present on the fiber surface or making possible their crosslinking.

Our earlier research resulted in developing effective methods of synthesis of bifunctional organosilicon derivatives (both polysiloxanes and silsesquioxanes) that contained in their structure groups capable of bonding to the substrate and fluoroalkyl groups showing surface activity. These compounds, when applied to the modification of glass, made it possible to create superhydrophobic coatings (Maciejewski et al. 2014a, b, 2015). However, in the case of glass surfaces and glass fibers (as well as mineral fibers), alkoxy groups easily undergo condensation due to the different character of the Si-OH groups on glass surfaces in contradistinction to the C-OH groups present on surfaces of natural fibers (Valdez-Gonzalez et al. 2009). This is why our study was aimed at determining the effect of the kind of organofunctional polysiloxane and the method of its application on the hydrophobic properties of cotton fabrics and on the possibilities of creating durable coatings resistant to multiple washings. Moreover, the objective of our study was a comparison of two methods of modification: (1) a one-step method via the chemical modification of fabrics with solutions of bifunctional polysiloxanes and (2) a two-step method—via preliminary modification of fabrics with silica sol followed by the chemical modification with solutions of bifunctional polysiloxanes.

Experimental

Materials

A cotton fabric with an areal density of 145 g/m² was supplied by the Textile Factory in Łódź (Poland).

Two types of bifunctional polysiloxanes with different ratios of functional groups (with the general formula shown in Fig. 1) were used.

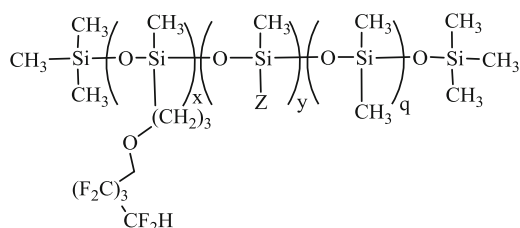
All of these compounds were synthesized according to the method described earlier (Maciejewski et al. 2014a, b). Tetraethoxysilane was obtained from “Unisil” (Tarnów, Poland). Other reagents and solvents were purchased from Aldrich.

Modification of cotton fabrics (C or CT)

The modification was performed by the one-step method via chemical treatment with solutions of bifunctional polysiloxanes or by the two-step method, which consisted of the introduction of silica sol at the first stage followed by the chemical modification. The durability of the hydrophobic properties of fabrics was determined by measurements of the WCA on the surface of fabrics after the modification and after one and ten washings at 40 °C for 1 h.

Chemical modification with polysiloxanes (S or ST)

In a round-bottom flask equipped with a reflux condenser and a magnetic stirrer were placed 5 vol% of isopropanolic solution of polysiloxane, 5 vol% of water and 5 vol% of acetic acid, and hydrolysis was



where: Z = CH₂CH₂Si(OC₂H₅)₃ and x=12; y=6; q=82 (1)

Z = CH₂CH₂Si(OC₂H₅)₃ and x=9; y=9; q=82 (2)

Z = CH₂CH₂Si(OC₂H₅)₃ and x=15; y=10; q=50 (3)

Z = (CH₂)₃OCH₂CH₂CH₂OCH₂ and x=15; y=10; q=50 (4)

Fig. 1 General formula of bifunctional polysiloxanes

conducted for 1 h at room temperature or at 80 °C. The obtained mixture was transferred into trays where bleached fabrics were impregnated for 15, 30 or 60 min. Then, the excess of the modifier solution was removed by squeezing followed by drying for 1 h at 80 °C and fixing for 3 min at 130 °C.

Modification with silica sol

In a round-bottom flask equipped with a reflux condenser and a magnetic stirrer was placed tetraethoxysilane (10 vol%) in water with the addition of 5 vol% of acetic acid, and hydrolysis was conducted for 1 h at 80 °C. Then, the mixture was transferred into trays, and the samples were soaked for 40 min at room temperature. After that time, excess modifier solution was removed by squeezing followed by drying for 2 h at 80 °C.

An alternative method for the preparation of the silica layer on the surface of fibers was the sol–gel process catalyzed by dibutyltin dilaurate. In a round-bottom flask equipped with a reflux condenser and a magnetic stirrer were placed tetraethoxysilane (20 vol%) in isopropanolic solution, water (0.9 vol%) and dibutyltin dilaurate (0.9 vol%) as a catalyst, and hydrolysis was conducted for 1 h at room temperature. Then, the mixture was transferred into trays, and the fabric samples were impregnated for 40 min. This was followed by the removal of the excess of the modifier solution by squeezing and drying for 2 h at 80 °C.

Determination of the amount of modifiers applied on fabrics (add-on)

The total dry solid add-on in cotton fabric samples (A) was determined by weighing a fabric sample before (W_i) and after (W_f) its modification with a composition used and thermal fixing. The analytical balance Ohaus was used for the measurements. The uptake (Table 1) was calculated according to the following equation:

$$A = \frac{W_f - W_i}{W_i} \times 100$$

Analysis of the elemental composition of the applied coatings

The analysis was carried out by employing the SEM-EDS technique to determine the ultimate elements (Si,

Table 1 Add-on of the modified samples

Modification method		Add-on
One step	C	6.4
	CT	6.6
Two step	S	7.5
Sol–gel catalyzed by acetic acid	ST	7.7
Two step	S	7.9
Sol–gel catalyzed by dibutyltin dilaurate		

F, N and P) present in the modifying mixtures. A Hitachi S-3500 N scanning electron microscope (SEM) equipped with an EDS (energy-dispersive X-ray) detector (Ultra Dry Silicon Drift X-ray Detector made by Thermo Scientific) was used for the measurements.

FTIR analysis

FTIR spectra of the modified fabrics were taken on a Bruker spectrometer, model Tensor 27, with a Specac Golden Gate single-reflection diamond ATR accessory.

Determination of hydrophobic properties

The water contact angles were measured using an automatic video contact-angle testing apparatus, the Krüss model DSA 100 Expert. A 10- μ l volume of water was applied to the treated cotton fabrics, and the contact angle was determined from the video camera images of the drop in the course of its formation. Each measurement is an average of five drops.

Studies of surface topography

The microscopic evaluation of surface changes of modified and unmodified samples of the cotton fabric was carried out using a Hitachi S-3400 N scanning electron microscope, where samples were coated with a thin layer of gold before performing observations. Moreover, SEM images were taken using an FEI Quanta 250 FEG instrument equipped with a large field detector (LFD) that records the secondary electrons (SEs). In the latter case (i.e., the LFD SE measurements), the samples were not covered by any layers. The microscope was operated at low vacuum mode (70 Pa), and the accelerating voltage was 10 kV.

Results and discussion

Two types of bifunctional polysiloxanes with the general formula shown in Fig. 1 were used in the study. Besides the fluoroalkyl groups, they also contained trialkoxysilyl or glycidoxypopyl groups capable of bonding to the substrate by the reaction with the OH groups in the one- and two-step processes.

The applied compounds differed in the length of polysiloxane chains and content of particular functional groups. Samples of fabrics were modified in a one-step process (chemical modification with a solution of organofunctional polysiloxane) or a two-step process (modification with the use of silica sol followed by chemical modification with the same solution of organofunctional polysiloxane). The modifications were carried out at room temperature and at 80 °C. For all the samples, measurements of the contact angle were conducted directly after the modification and after washing. Moreover, the weight of all samples after their modification was determined and the add-on calculated. The add-on differs depending on the modification method employed (Table 1). However, the differences are mainly caused by the modification procedure, i.e., whether the modification proceeded in one or two steps. No substantial effect of temperature on the add-on value was observed. The kind of polysiloxane also did not influence the add-on values, and the dispersion of the latter for different polysiloxanes was ± 0.1 . This is why the results shown in Table 1 are the mean values for the modification with the polysiloxanes studied by using a given method of modification.

The greatest add-on was found in the case of the samples impregnated with tetraethoxysilane using dibutyltin dilaurate as a catalyst, whereas a smaller add-on was observed on the fabrics subjected to chemical modification only (C or CT). The reason for the greatest add-on in the former case should be sought in the TEOS concentration, which was twice as high as that in the other method of silica sol preparation. Nevertheless, the differences in add-on values between all samples studied are not large.

At the initial stage of the study, the effect of the modification process duration on hydrophobic properties was determined. To this end, the modification with polysiloxane 1 (in the one-step and two-step process) was conducted for 15, 30 and 60 min, and WCA on such a modified surface was measured before and after washing (Figs. 2, 3, respectively).

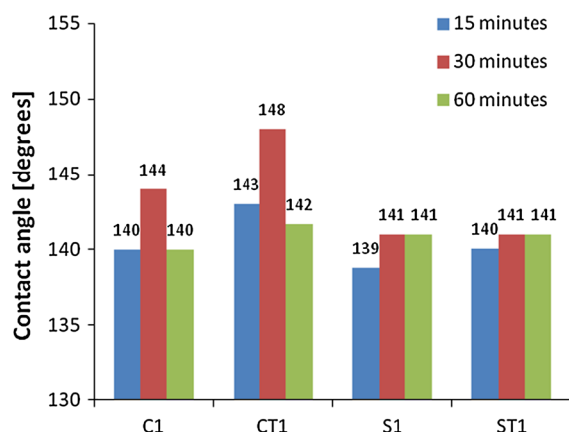


Fig. 2 Water contact angles on the cotton fabric surface before washing for different durations of the modification with polysiloxane **1**. C1, one-step process at room temperature; CT1, one-step process at 80 °C; S1, two-step process at room temperature; ST1, two-step process at 80 °C

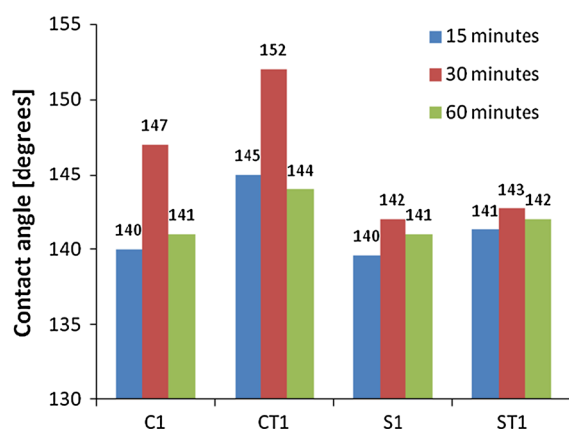


Fig. 3 Water contact angles on the cotton fabric surface after washing for different durations of the modification with polysiloxane **1**. C1, one-step process at room temperature; CT1, one-step process at 80 °C; S1, two-step process at room temperature; ST1, two-step process at 80 °C

The obtained results of the contact angle measurements show that all the modified samples are strongly hydrophobic. Furthermore, in the case of one-step modified fabrics (i.e. only by impregnation in solutions), such high WCA values as those achieved for the samples C1 and CT1 are very rarely obtained. In most of the hitherto published papers, the obtained WCA values for surfaces modified only with chemical compounds (without additional treatment of the surface) are in the range 95°–115°. However, in most

cases the modifiers were molecular compounds, mainly organofunctional silanes and not polysiloxanes. Recently, a report appeared on the modification of cotton fabrics with the use of 1H, 1H, 2H, 2H, fluorooctyltriethoxysilane or Fluorolink (a commercial product) in both the one-step and two-step process (using tetraethoxysilane), which resulted in an impressive value of WCA = 169° (Ferrero and Periolatto 2013). To achieve such a high WCA value, it was necessary to conduct the impregnation for 24 h, because a shorter impregnation time resulted in a WCA value comparable to that obtained by us. However, after the washing process the mentioned WCA decreased, contrary to the WCA on our sample that increased after washing.

The optimal duration of the modification is 30 min. A longer modification time leads to a reduction in the WCA value, most likely as a result of the condensation of polysiloxane itself or the deposition of too many layers on the fiber surface. Moreover, a higher temperature of the process favors a more efficient hydrolysis and condensation on the fiber surface as results from the fact that in all cases higher values of the contact angle were observed for the modification proceeding at 80 °C, when it was carried out as both the one-step or the two-step process.

Furthermore, one can notice that the contact angle values increased after washing (Fig. 3), which testifies to the durability of the modification performed and also shows that the washing process facilitates the condensation of those groups that were not fully bound to the surface and makes the removal of the compounds that were only occluded easier. During the washing process a reorganization of fluoroalkyl groups and their better orientation on the fiber surface can occur, which is reflected by the higher WCA values. In the case of the CT1 sample, the superhydrophobic surface was obtained after washing, but most of the obtained WCA values are close to the cutoff point for superhydrophobicity, i.e., 150°. The WCA values obtained after one washing remained unchanged after ten subsequent washings. Somewhat surprising were the lower (although still high) values of WCA obtained for two-step modified fabrics, which in the first step were covered with silica sol.

On the basis of the obtained results, modifications with subsequent polysiloxanes were performed, namely, the duration of the modification with a solution of an appropriate polysiloxane was 30 min.

Figure 4 shows the contact angles on fabrics before and after washing, modified by the one-step and the two-step process at room temperature and at 80 °C.

The above results are very close to those obtained for fabrics modified with polysiloxane **1**. For both polysiloxanes, the highest values of the contact angle have been obtained for the one-step modified fabric at 80 °C. An additional fixation of the coating after the washing process was also observed (WCA values remained on an unchanged level after ten washings). While comparing the values of the contact angle for fabrics modified with polysiloxanes **1** and **2**, one can notice a slight increase in the contact angle value in the case of polysiloxane **1**. The aforementioned compounds differ in the fluoroalkyl group content, whereas the length of their polysiloxane chains is the same. A higher fluorine content in compound **1** finds its reflection in the increased contact angle, although the difference is very small. This means that the number of fluoroalkyl groups does not have a significant effect on the observed hydrophobic properties. This finds some confirmation in the results obtained for the fabric modified with the use of polysiloxane **3**, which has an even higher fluorine content (Fig. 5).

Despite a higher content of fluoroalkyl groups, the contact angle did not increase (it is even slightly smaller). On the other hand, the chain of polysiloxane **3** is shorter than those of polysiloxanes **1** and **2**. It contains a smaller number of dimethylsiloxane groups

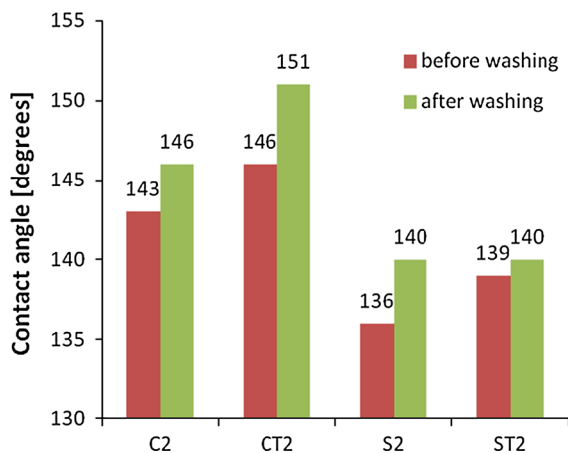


Fig. 4 Water contact angles on the cotton fabric surface, before and after washing, modified with a solution of polysiloxane **2**. C2, one-step process at room temperature; CT2, one-step process at 80 °C; S2, two-step process at room temperature; ST2, two-step process at 80 °C

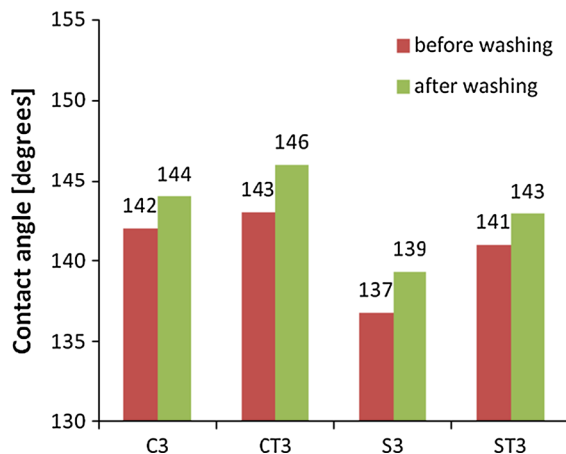


Fig. 5 Water contact angles on the cotton fabric surface, before and after washing, modified with a solution of polysiloxane **3**. C3, one-step process at room temperature; CT3, one-step process at 80 °C; S3, two-step process at room temperature; ST3, two-step process at 80 °C

($-\text{OSi}(\text{Me})_2-$), which also impart hydrophobic properties to the modified surfaces. Taking into consideration a very good orientation of the polysiloxane on the surface, one can suppose that a longer chain with a smaller content of functional groups (derivatives **1** and **2**) will cause a better orientation of fluoroalkyl groups on the surface than polysiloxane **3**, which contains a higher number of functional groups attached to a shorter chain.

Our earlier studies on the modification of glass surfaces have shown that very good hydrophobizing effects can be obtained with the use of glycidopropyl group-containing polysiloxane. These groups can react with surface hydroxyl groups, and, moreover, due to a longer chain compared to trialkoxysilyl group (present in polysiloxanes **1–3**), they can cause a greater diversification of the surface (Maciejewski et al. 2014a, b). In Fig. 6 the contact angle values are presented for the fabric modified with polysiloxane **4**, before and after its washing.

The obtained results have not confirmed the tendency observed in the case of the modification of glass surfaces. However, this is the effect of the different nature of hydroxyl groups on the fiber surface. The oxirane ring (in the glycidyl group) easily undergoes a rupture under the influence of hydroxyl groups ($-\text{Si}-\text{OH}$ on a glass surface) because of the acidic nature of the proton from this group, contrary to the hydroxyl groups $\text{C}-\text{OH}$ on the fiber

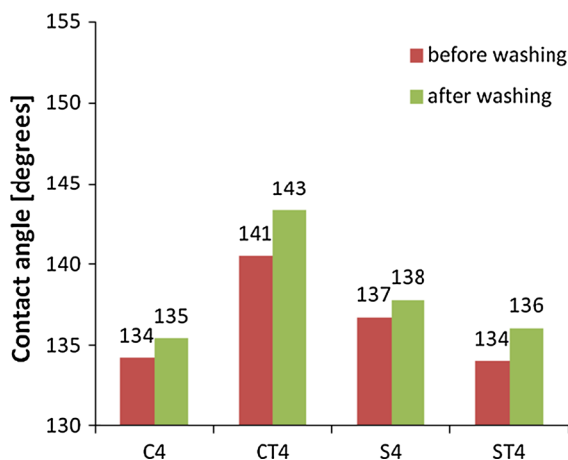


Fig. 6 Water contact angles on the cotton fabric surface, before and after washing, modified with a solution of polysiloxane **4**. C4, one-step process at room temperature; T4, one-step process at 80 °C; S4, two-step process at room temperature; ST4, two-step process at 80 °C

surface. Nevertheless, the differences are not significant, which shows that the derivatives of this type can also be applied to the modification of fibers. In each of the above cases, one can notice that the WCA values for the two-step modification are worse than those obtained for the one-step modification, which is a big surprise.

To confirm the durable attachment of modifiers to the fiber surface, an FTIR analysis was been performed. In Fig. 7, the spectra of the unmodified and modified fabrics subjected to chemical modification with polysiloxanes **1** and **4** are compared. Polysiloxane **1** was chosen for the analysis because of its best hydrophobic effect and polysiloxane **4** for the sake of comparison (because of the presence of glycidyl groups). In the visible spectra are differences resulting from the attachment of the organosilicon compound to cellulose hydroxyl groups. The band at 3330 cm^{-1} , which is characteristic of the free OH groups present on the fiber surface, is slightly smaller, which indicates bonding between the fiber and alkoxy-silyl groups. Moreover, the spectra of the modified samples contain bands at about 800 and 1260 cm^{-1} , originating from Si–O–Si symmetric stretching vibrations and Si–O–C stretching vibration shoulder, respectively.

The band expected at 1018 cm^{-1} (Si–O–Si) is overlapped with a broad band between 950 and 1100 cm^{-1} , attributed to the characteristic peaks of cellulose. It is worth mentioning that the spectra of

unwashed and washed samples have an analogous shape, which testifies to the durability of the modifications performed. In the spectra, differences are visible, resulting from the attachment of organosilicon compounds to the cellulose hydroxyl groups. The band at 3330 cm^{-1} is slightly smaller, which indicates bonding between the fiber and alkoxy-silyl groups. Moreover, the spectra of the modified samples contain bands at about 800 and 1260 cm^{-1} , the origin of which was mentioned above. The band expected at 1018 cm^{-1} (Si–O–Si) is overlapped with a broad band between 950 and 1100 cm^{-1} attributed to the characteristic peaks of cellulose. It is worth mentioning that the spectra of unwashed and washed samples have an analogous shape, which testifies to the durability of the modifications performed.

To further confirm the presence of hydrophobizing compositions on fabrics, analyses have been performed for the content of selected elements on the surface of modified fabrics by using the SEM EDS technique. The elemental composition of surfaces of unmodified fabric (**0**) and fabrics modified with polysiloxanes **1** or **4** (chemical modification only), unwashed and subjected to washing (W), is presented in Table 2.

The obtained results unequivocally point to the presence of elements characteristic of the polysiloxanes employed and confirm the effectiveness of the modification performed. Silicon and fluorine contents determined after multiple washing are close to those before washing, which testifies to a durable attachment of modifiers to the fiber surfaces. Fabrics impregnated with the composition containing polysiloxane **4** contain more fluorine than those modified with polysiloxane **1**, which results from the higher fluorine content in polysiloxane **4** used for the impregnation. However, despite the higher fluorine content, WCA on this fabric appeared to be smaller, as was already mentioned.

Morphological analysis of the fiber surface with the use of SEM, performed before and after the modification (both by the two-step and one-step process), showed significant differences (Fig. 8). The unmodified fibers (Fig. 8a) have the typical longitudinal fibril structure, whereas the fibers covered with organofunctional polysiloxane (in the single step process) show a homogeneous coating on the entire length of fibers (Fig. 8b). On the other hand, after the modification with silica hydrosol (Fig. 8c), SiO_2 clusters were observed, which were incorporated in the structure of fibers, making their surface heterogeneous.

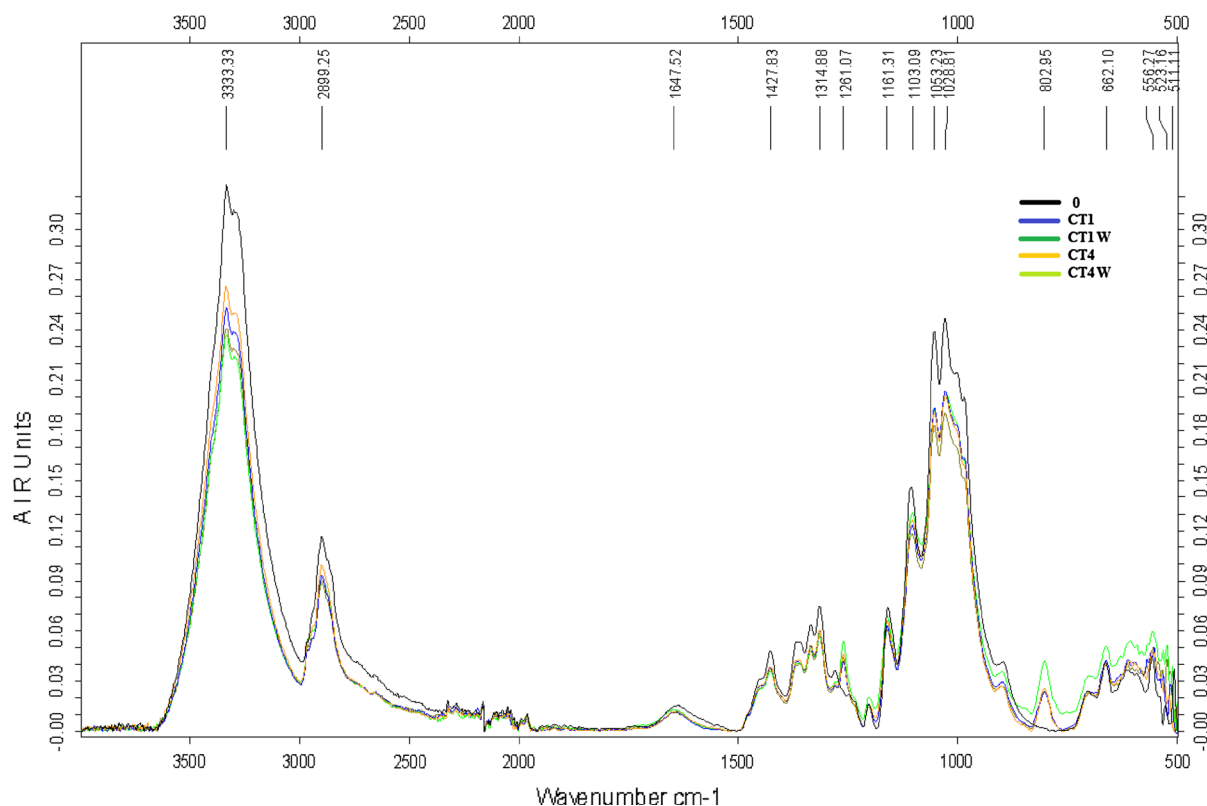


Fig. 7 FTIR spectra of unmodified fabric and fabrics modified in the one-step process with polysiloxanes **1** and **4**, before and after washing (W)

Table 2 Results SEM EDS analysis of modified samples

Code	C (%)	O (%)	Si (%)	F (%)	Other elements
0	34.2 ± 0.2	64.8 ± 0.4	0.3 ± 0.1	–	0.7 ± 0.1
CT1	33.3 ± 0.2	59.8 ± 0.4	3.3 ± 0.2	2.9 ± 0.3	0.7 ± 0.1
CT1(W)	33.4 ± 0.2	59.5 ± 0.4	3.4 ± 0.2	3.1 ± 0.2	0.6 ± 0.1
CT4	33.3 ± 0.2	58.9 ± 0.4	3.2 ± 0.2	4.0 ± 0.1	0.6 ± 0.2
CT4(W)	33.1 ± 2	58.8 ± 0.4	3.4 ± 0.1	4.1 ± 0.3	0.6 ± 0.2

The above analysis has shown a patchy distribution of silica on the fabric, which could be caused by a prior condensation of silica molecules (and their agglomeration) during hydrolysis. The sol–gel process was carried out in the presence of acetic acid as a catalyst; therefore, we decided to change the catalytic system and to apply dibutyltin dilaurate (DBTDL). The other conditions of the process remained unchanged. The fabric modified in such a prepared sol was subjected to SEM analysis. The analysis was performed for surfaces before and after washing, and the relevant micrographs are presented in Fig. 9a, b, respectively.

The SEM images confirm that the change of catalyst for the sol–gel process has a very good effect on the fiber surface morphology. The silica layer envelopes the fibers as results from the micrographs that show a clear layer without any presence of agglomerates. For this reason, we repeated the two-step modification at room temperature involving all the investigated polysiloxanes in turn and using the silica hydrosol obtained in the sol–gel process catalyzed by DBTDL. The WCA values obtained for each of the studied surfaces are shown in Fig. 10.

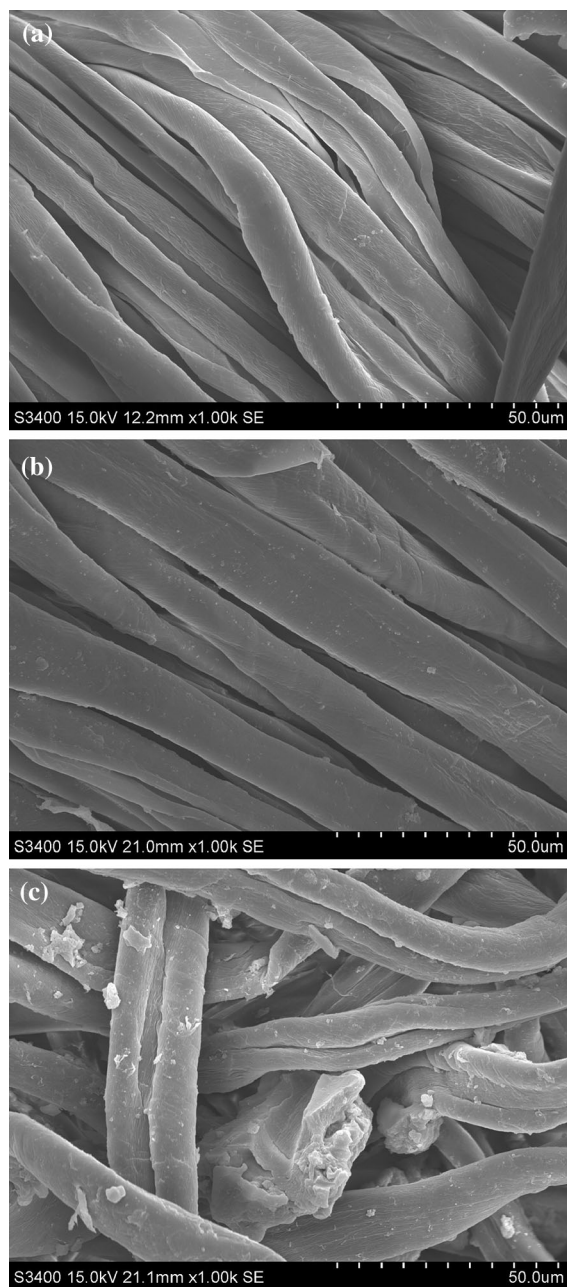


Fig. 8 SEM images of the surface of fibers, **a** unmodified, **b** chemically modified with the solution of polysiloxane **1**, **c** modified with silica hydrosol

The change of catalyst for the sol–gel process, despite a better surface morphology, did not cause a considerable increase in WCA values (a rise by just a few degrees), which means that the method of silica sol preparation is not of significant importance. The application of silica on surfaces (including the surface

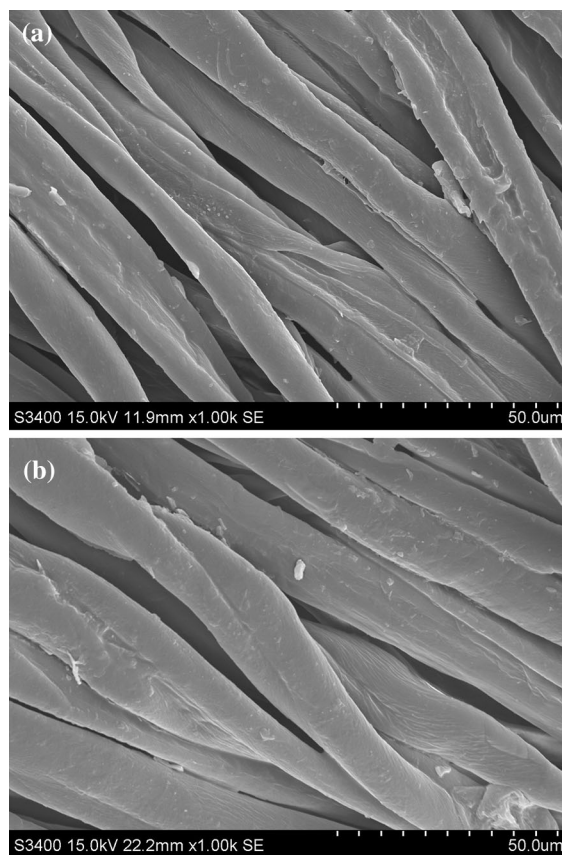


Fig. 9 SEM images of surfaces of fibers modified with silica hydrosol using DBTDL as a catalyst, **a** before washing, **b** after washing

of fibers) is aimed at increasing surface roughness. However, in our case the polymer layer played an analogous role. The application of organofunctional polysiloxanes to the chemical modification made it possible to form a homogeneous polymeric layer along a fiber and at the same time to create chemical bonding via reactive groups. It is worth mentioning that the small number of groups that anchor polysiloxane to the substrate caused the remaining part of the polysiloxane chain, because of its flexibility, to undergo bending that resulted in the surface diversification and exposition of fluoroalkyl groups to the outside (see Scheme 1).

This is why polysiloxane **1** has better properties than polysiloxane **2**, because the former contains more fluoroalkyl groups and fewer trialkoxysilyl ones (at the same chain length), and this makes it more flexible and capable of better bending. On the other hand, both of

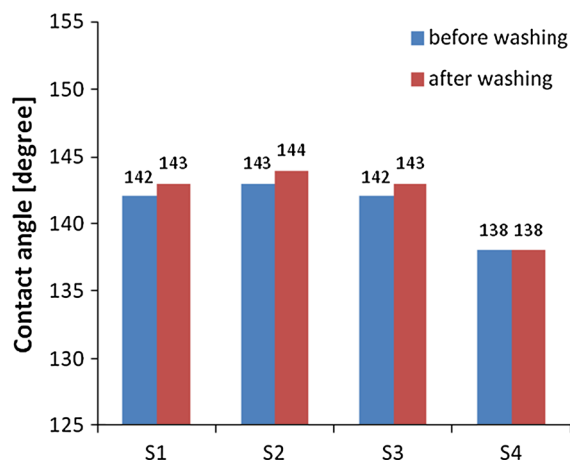


Fig. 10 Water contact angles on the cotton fabric surface before and after washing, modified by the two-step method at room temperature with the use of silica hydrosol and S1, polysiloxane 1; S2, polysiloxane 2; S3, polysiloxane 3; S4, polysiloxane 4

the aforementioned derivatives enabled obtaining higher WCA values than did polysiloxane 3, because the latter contains more functional groups (besides a shorter chain), and thereby it is more rigid. In the case of the two-step modification, the organofunctional polysiloxane applied on the silica layer (that was deposited prior to polysiloxane) tightly adheres to it because of a greater compatibility to the layer than to pristine fibers (this results from the different nature of hydroxyl groups, as was mentioned earlier). As a result of this fact, the hydrophobic character of such a modified surface becomes weaker because the introduced polymeric layer smoothes down the surface with deposited silica. Thereby an opposite effect is visible compared to that observed after the modification of the silica layer with organofunctional silanes, which, while bonding pointwise, cause an increase in hydrophobicity.

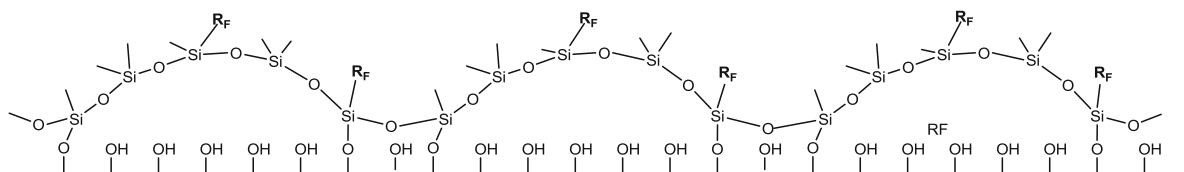
We also made an attempt at analyzing the surface topography of fibers using atomic force microscopy. Unfortunately, we did not obtain unequivocal results because of the too high roughness of the studied fabric and the local character of the measurements that did

not give the entire picture of the fabric. For this reason, we applied SEM with the use of an LFD (SE) detector to confirm the coating of the modified fabrics, and this time the attempt appeared successful because the observations of the samples provided evidence for covering the fiber surfaces (Fig. 11).

In the image of the unmodified sample (Fig. 11a), only a clean fiber structure can be seen. The surface of each fiber is smooth, but fine terraces are visible on the fiber cuticle, and this is typical for cotton. In the case of the sample chemically modified with the solution of polysiloxane 1 (Fig. 11b), each fiber contains additional material on the thread surface. On the fiber surface, additional structures of sizes from 200 to 5000 nm are visible, which often have sharp geometric edges, and many of them have an elongated shape. The image of the sample subjected to washing (Fig. 11c) does not show any significant change in the amount of polysiloxane 1 deposited on fibers. The surface of fibers is evenly coated with a polysiloxane layer, which confirms the earlier observations.

The conducted study showed that the one-step modification gives much better effects and makes it possible to obtain fabrics with strongly hydrophobic or even superhydrophobic properties. These properties are durable and are maintained after ten washings.

Moreover, all the one-step modified samples and the two-step modified ones (i.e., those where the sol-gel process was catalyzed by DBTDL) were subjected to the determination of their hygroscopicity. The measurements were carried out in compliance with the standard JIS 1090:1990 “Water drop absorption.” The time of maintaining a water drop on the surface of a bleached fabric was 1.43 s, whereas on surfaces of all other samples it exceeded the maximum value given in the standard, i.e., 1800 s. In the case of our modified fabrics, this parameter is significantly better than in that of fabrics described in the literature (Ferrero and Periolatto 2013) for which the absorption time after washing was shorter than 1 min, in spite of very high WCA.



Scheme 1 An example of organofunctional polysiloxane orientation on the fiber surface (where $R_F = (CH_2)_3OCH_2(CF_2)_3CF_2H$)

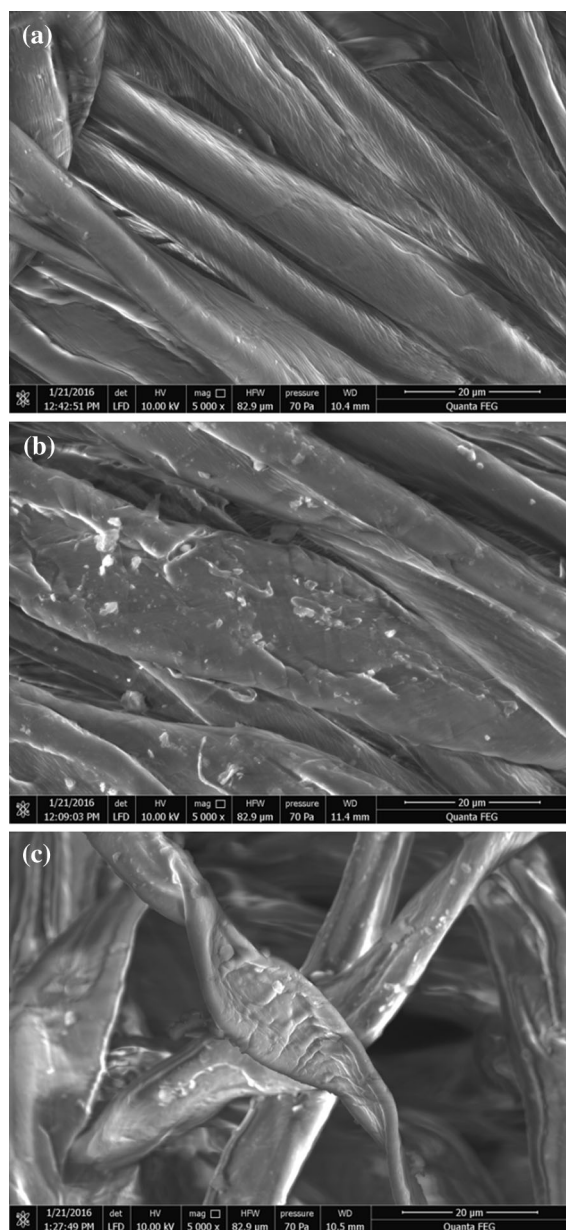


Fig. 11 SEM (LFD SE) images of the surface of fibers, **a** unmodified, **b** chemically modified with the solution of polysiloxane **1**, **c** chemically modified with the solution of polysiloxane **1** after washing

None of the one-step modifications affected the appearance and structure of fabrics. The samples preserved their soft hand and had not changed their color, and no loss of the modifier layer and hardening were observed. Additionally, a preliminary study was conducted on the strength of the modified fabrics. The obtained results showed no differences in strength

compared to the unmodified fabric. However, research on this aspect is underway and will be the subject of another paper.

Conclusions

The study showed that bifunctional polysiloxanes containing fluoroalkyl groups (those imparting surface properties) and trialkoxysilyl or glycidyl groups (those bonding to substrates) are very good hydrophobizing agents. A very simple one-step method of fabric modification was developed (by impregnation in solutions of the aforementioned polysiloxanes). The method makes it possible to produce superhydrophobic fabrics, properties of which are durable even after multiple washings (Maciejewski and Przybylak 2015). The employed polysiloxanes, because of the specific properties of siloxane chains (flexibility and capability of orienting on the surface) as well as the presence of suitable functional groups, can durably attach to the fiber, thus forming a homogeneous strongly hydrophobic (due to the presence of fluoroalkyl groups) layer on its surface. The production of superhydrophobic washing-proof fabrics, characterized by a very long time of water absorption (also after washing process), by chemical modification (without an additional modification or activation) was not possible until recently. Currently, because of the application of bifunctional polysiloxanes, fabrics with such properties can be produced in a cheap, simple and fast (30 min impregnation) way.

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