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Durable and highly hydrophobic flax fabrics designing via “grafting to” method using catalysed hydrosilylation

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A B S T R A C T

Highly hydrophobic flax fabrics with durable properties were prepared via “grafting to” method for self-cleaning application. Flax fabrics were firstly functionalized with vinyl groups using 1,3-divinyltetramethyldisilazane (DVTS). Then, the vinyl functionalized flax fabrics were grafted by poly(hydromethylsiloxane-co-dimethylsiloxane) (PDMS-co-PHMS) via a hydrosilylation reaction using Karstedt catalyst, between Si-H groups present in PDMS-co-PHMS and vinyl groups present onto the vinyl functionalized flax fabrics. The prepared fabrics were characterized using Fourier-transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), X-rays fluorescence, confocal laser scanning microscopy (CLSM) and tensile test. The modified fabrics displayed highly hydrophobic properties with contact angle (θ) about $147^\circ \pm 5$ and a sliding angle (SA) of about $15^\circ \pm 2$, making them ideal for practical self-cleaning applications. Furthermore, good durability with excellent washing resistance was also obtained for these fabrics.

Keywords:

Flax fabric
Silicone/silazane
Hydrophobic
Self-cleaning
Hydrosilylation
Grafting to

1. Introduction

Hydrophobic fabrics have attracted a lot of attention in academic and industrial fields due to their wide applications [1], such as oil-water separation [2–7] or self-cleaning [8–13]. Moreover, in some studies, additional applications like flame retardant [14–16], antifouling [17] and UV-shielding [18–20] have been mentioned. Up to date, there are many methods that have been applied to successfully impart hydrophobic properties to natural fabrics, such as dip-coating [4,21], spray coating [22,23] and layer-by-layer assembly [16]. However, many hydrophobic fabrics tend to lose their hydrophobicity over time due to the weak interfacial interaction between hydrophobic layer and fabric fibers [24–26]. Thus, a durable hydrophobic natural fabric is a great challenge for many applications. Generally, creation of covalent bonds between the hydrophobic compounds and the fabric surface is one of the most effective method to improve the durability of hydrophobic fabrics [27, 28]. Usually, there are two ways to bond covalently polymer chains onto substrates. The first one is the “grafting from” method, also called surface-initiated polymerization. In this case, polymer chains grow from initiation sites on the fabric surface [29,30]. These sites could be generated by chemical etching [31], E-beam irradiation [32] or plasma /

ionizing treatments [33]. As an example, Li et al. [34] have grafted short fluoroalkyl chains on cotton fibers via atom transfer radical polymerization (ATRP) strategy to design superhydrophobic cotton fabrics. The treated cotton surfaces demonstrated highly hydrophobic properties with a contact angle of about 163° with excellent stability under washing process.

The second way is the “grafting to” method where pre-formed polymer is grafted on the substrate via reactions between functional groups of the polymer chains and the surface of the substrate [35]. This method has the advantages to limit the amount of used compound during the functionalization steps and has usually a higher grafting rate than the “grafting from” method. Indeed, due to the poor initiator density on the fiber surface, “grafting from” method has often low polymerization rates [36]. In our knowledge, hydrosilylation reaction has not yet been used to graft polysiloxane compounds onto the surface of natural fabrics, the classical strategies for this purpose are usually sol/gel reaction [28,37,38] and plasma treatment [39]. For example, Deng et al. [40] have grafted a polyhedral oligomeric silsesquioxane (POSS) bearing a trimethoxysilane function (MPTMS) onto cotton fabric via sol/gel reaction to form a stable and robust hydrophobic layer. The modified cotton fabric displayed good hydrophobic properties with a

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value of water contact angle higher than 142°. Due to the covalent bonds between the POSS part and the fabric surface, the modified cotton fabric showed an excellent resistance to chemical and ultrasonic washing.

Polydimethylsiloxanes (PDMS) are widely used to prepare hydrophobic fabrics [2–6,41]. Indeed, their optical transparency and low surface energy have made them an attractive route for the fabrication of materials with hydrophobic surfaces [42]. Thus, it would be useful to prepare a hydrophobic flax fabric by grafting PDMS onto fibers structure to support the durability of its hydrophobic properties.

In this study, surface treatment was used to prepare highly hydrophobic and durable flax fabrics via a “grafting to” method. Firstly, flax fabrics were modified using 1,3-Divinyltetramethyl-disilazane (DVTS) in order to functionalize the fabric surface with vinyl groups, following the strategy developed previously in our team [43]. Then, Methylhydrosiloxane - dimethylsiloxane co-polymer (PDMS-co-PHMS) containing Si–H groups was grafted onto the fabric via a hydrosilylation reaction between Si-H and vinyl groups using Karstedt catalyst. The treated fabrics were characterized by FTIR and EDS spectroscopies. The Si content in the samples was measured using X-ray fluorescence. The hydrophobic and self-cleaning properties of the treated fabrics have been confirmed. Also, the treated fabrics exhibited excellent washing resistance, confirming the good durability of this grafting process. Moreover, the tensile test was performed on the obtained grafted fabrics to evaluate the impact of the grafting process on the mechanical properties.

2. Materials and methods

2.1. Materials

1,3-Divinyltetramethyl-disilazane (DVTS, 97 %), octamethylcyclotetrasiloxane (D₄, 97 %), poly(hydromethylsiloxane(25–35 %)–co-dimethylsiloxane) co-polymer trimethylsiloxane terminated (25–35 cSt, M_n = 2000 g/mol), were purchased from ABCR. Platinum-divinyltetramethyldisiloxane complex 2 % Pt in xylene (Karstedt catalyst) was bought from Gelest. Dimethylsulphoxide (DMSO, 99.9 %) and toluene (99.8 %) were supplied by Sigma-Aldrich. Acetone (99 %), and glacial acetic acid (99.5 %) were purchased from Fisher Scientific Co. Sodium hydroxide (NaOH, 98.5 %) was purchased from PanReac AppliChem. Liquid detergent contains 5–15% of anionic surfactants, 5 % of non-anionic surfactants, amphoteric surfactants and enzymes was supplied from Enzpin. All these chemical products were used without further purification. Flax fabric was obtained from Hexcel (France). The composition of flax fibers is 81 wt% of cellulose, 13 wt% of hemicellulose and 2.7 wt% of lignin in good agreement with the literature [44].

2.2. Preparation of functionalized flax fabric with vinyl groups

In our previous work [43], a grafting procedure using 1,3-divinyltetramethyl-disilazane (DVTS) was developed in order to prepare short flax fibers functionalized with vinyl groups. The same process was applied in this study to functionalize flax fabrics. The obtained fabric in this step is called (F/Si-vinyl).

2 g of pristine flax fabric (F/pristine), about 2 pieces of 7 × 7 cm² were dipped into 200 mL of NaOH solution (0.5 M) at 70 °C for 3 h under stirring. Then, a neutralization process was performed with 200 mL of acetic acid (0.6 M) for 30 min at 70 °C followed by washing with deionised water to remove all acetic acid traces. This first step is an alkaline treatment to remove lignin from flax fabrics, the obtained fabric in this step is called (F/pre-treated). Then, 4 g of DVTS was dissolved in 16 g of DMSO/Toluene (35/65 wt%) solvent mixture. The prepared solution was added into a bottom flask of 50 mL fitted with a reflux condenser. Then, 0.6 g of F/pre-treated (3 pieces of 3 × 3 cm²) was dipped in this solution for 3 h at 80 °C under stirring. Finally, the fabric samples were filtered and washed twice with 20 mL of toluene over 10 min to remove unreacted silazanes.

After reaction, the obtained flax fabrics are functionalized with vinyl

groups via Si-O-C covalent bonds due to the reaction between DVTS and hydroxyl groups of the flax fabrics (Fig. 1).

2.3. Preparation of flax fabric grafted with PDMS-co-PHMS

1 g of PDMS-co-PHMS was dissolved in 19 g of acetone with 0.1 mL of Karstedt catalyst using a closed flask of 50 mL. Afterwards, 0.6 g of F/Si-vinyl were dipped in this solution for 16 h at room temperature under stirring at 100 rpm. Finally, the fabric was filtered, squeezed by paper towel and washed twice with 20 mL of acetone over 10 min to remove unreacted and non-grafted molecules. It is worth noting, controlling the rate of grafted PDMS-co-PHMS is possible by adjusting the concentration of the treatment solution.

After the hydrosilylation reactions, grafted flax fabrics, called F/PDMS-co-PHMS, were obtained (Fig. 1).

Indeed, the hydrosilylation reaction corresponds to the addition of silicon-hydrogen bonds (Si–H) via a vinyl group (C=C) using platinum catalysts and typically follows the Chalk–Harrod mechanism [45,46] (Fig. 2).

This reaction allows to create a covalent bond between the F/Si-vinyl surface and the siloxane derivatives compounds.

3. Measurements

3.1. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectra of fabrics were obtained using a Bruker VERTEX 70 spectrometer. Attenuated total reflectance mode was used, by performing 32 scans between 400 and 4000 cm⁻¹ with a resolution of 4 cm⁻¹.

3.2. Confocal scanning microscopy

The characterization of fabrics surface was performed by confocal chromatic technology. The apparatus is composed of a CCS Prima Controller equipped with an OP1000 optical head (STIL SA, France). The device is controlled by Surface Map software. The optical sensor OP1000 had a 1 mm range.

4 areas of 700 × 700 μm with a lateral path of 0.5 μm were measured for each sample.

The signal was post processed with mountains MapV10 software (DigitalSurf, France). Some numerical operations have been carried out: levelling, extraction of interesting zones, and thresholding.

This analysis allows to measure the developed interfacial area ratio which is referred as the standard dimension ratio (Sdr %).

Sdr % allows the comparison of different fabrics regarding their surface roughness [47]. It describes the difference between the developed (true) and the projected surface area in percent according to Equation 1.

$$\text{Sdr \%} = \frac{A_{\text{developed}}}{A_{\text{projected}}} \times 100 \quad (1)$$

Sdr = 0 for a totally flat and smooth surface.

3.3. Scanning electron microscope coupled with energy dispersive X-ray spectrometer (SEM-EDS)

The cross section of grafted flax fabrics was analysed via scanning electron microscope (FEI Quanta 200). After being cut with a single edge blade, the samples were placed on a vertical sample holder under high vacuum at a voltage of 12.5 kV and a working distance of 10 mm. To locate the presence of the silicon element which represents the grafted molecules into fabric, SEM analysis was coupled with an energy dispersive X-ray spectroscopy, EDS, (Oxford INCA Energy system).

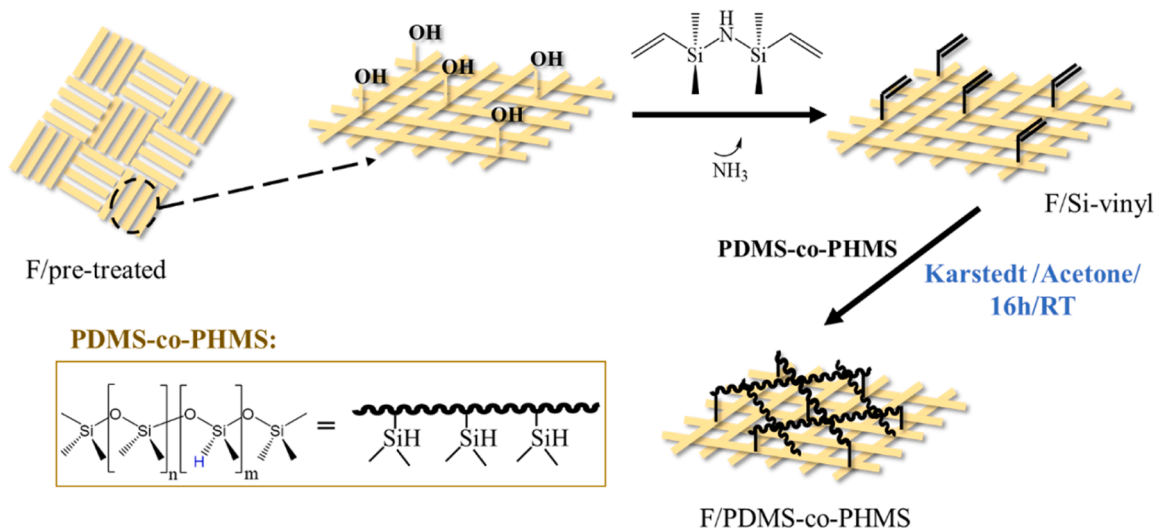


Fig. 1. Schematic representation of the reaction of DVTS with hydroxyl groups of the flax fibers and the reaction between Si-H and vinyl groups to produce PDMS-co-PHMS-grafted fabric (F/PDMS-co-PHMS).

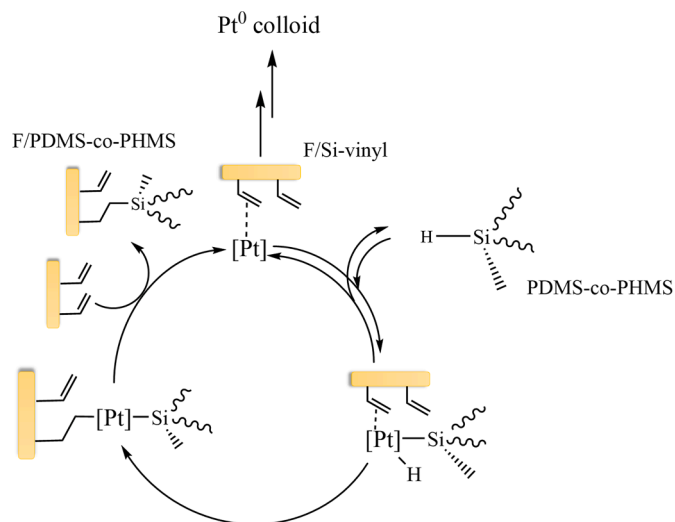


Fig. 2. Suggested mechanism of the hydrosilylation reaction of vinyl group onto flax fabric by Si-H group in PDMS-co-PHMS, inspired from [46].

3.4. X-ray fluorescence elemental analysis

Silicon content in flax fabrics samples was determined using an Oxford XMET 5100 X-ray fluorescence. Samples were fixed on a flat polymer-based support containing no trace of silicon. This holder is used to flatten fabric sample in order to reduce instrumental errors. The analyses were carried out under atmospheric pressure, without any preparation. The following settings were used by default: 13 kV and 45 μ A. Each spectrum was collected for 1 min. The intensity of the Silicon peak is proportional to its concentration in the fabric sample. The measurement was carried out 3 times for each sample.

To obtain calibration curve, a series of octamethylcyclotetrasiloxane (D₄) solution with four different concentrations (1, 6, 12, 20 wt%) was prepared using THF as a solvent. Then, four pieces of flax fabric (2 \times 2 cm²) were immersed in each solution for 3 min, these samples were defined as standards. Afterwards, the flax fabric samples were dried under the hood for 1 hour. The mass gain of each sample was calculated using equation 2:

$$\text{Mass gain wt\%} = \frac{(\text{Initial weight of sample}) - (\text{Final weight of sample})}{(\text{Final weight of sample})} \times 100 \quad (2)$$

Then the mass gain of each sample was transformed to Silicon content using equation 3:

$$\text{Si wt\%} = \frac{(\text{Mass gain\%}) \times 4 (\text{number of Si in D}_4) \times (\text{Molar mass of Si})}{(\text{Molar mass of D}_4)} \quad (3)$$

The four samples were analysed using an X-ray fluorescence spectrometer to determine the fluorescence intensity of each one (Figure S1). The values of fluorescence peak areas of Silicon element for the standard samples were drawn as a function of Silicon content in order to obtain a calibration curve with a linear equation (Eq 4). This equation was then useful to determine the silicon content of unknown samples from direct X-ray fluorescence spectrometry analysis.

$$X = \frac{Y + 20.8}{32.8} \quad (4)$$

where X is the Silicon content (wt%) of the sample and Y is the value of fluorescence peak area.

3.5. Contact angles (θ) and sliding angles (SA) measurement

A Krüss DSA 30 apparatus was used to measure the contact angles (θ) of water on the samples surface. The measurement was done 3 times in 5 different zones for each grafted fabric sample with 3 μ L drops of water. The sliding angles (SA) were measured using a lab-made device. The device is a vertical metal axis crossed with a manually movable horizontal one which holds a protractor on the side and a sample carrier on the top. The treated flax fabric is placed on the sample carrier and a drop of water (50 μ L) is put on the fabric surface. The horizontal support is then slowly tilted until the water drop rolls over the fabric surface. The SA is taken as the value of the angle from which the water drop begins to slip out of the sample surface.

3.6. Durability tests

3.6.1. Washing test

Three samples of F/PDMS-co-PHMS (0.6 g) were washed in 100 ml of detergent solution 2 g/L at 40 $^{\circ}$ C for 10 min under stirring (200 rpm).

This test is a lab-simulation of a home wash [15]. Then, the solution was removed and the fabric underwent several washes with deionised water to remove all traces of the detergent solution. The washing cycle was repeated 10 times for each fabric sample. X-ray fluorescence elemental analysis was used to assess the evolution of silicon concentration with the washing cycles.

3.6.2. Acid resistance test

This test was performed in order to verify the stability of the chemical treatment at the fabrics surface [48], knowing the siloxane sensitivity to the acid media. Three samples of F/PDMS-co-PHMS (0.6 g) were immersed in 100 ml of HCl solution (0.01 M, pH = 2) for 3 h at room temperature. Then, the samples were washed with deionized water to remove HCl traces. The X-ray fluorescence elemental analysis was also used to detect the loss of silicon element during the washing cycles.

3.6.3. Tensile test

The fabric thread underwent a tensile test using a Zwick/Roell tensile machine, which was fitted with a 2.5 kN load cell and a clip-on extensometer with a 30 mm reference length. This test was conducted under room temperature conditions (25 °C), and the equipment was calibrated in accordance with ISO 7500-1 and ISO 9513 standards for force and displacement sensors, respectively.

A crosshead speed of 10 mm/min was employed, with a pre-charge of 1 N applied. The determination of Young's modulus was accomplished using the tangent method within the range of 0.5 % to 2 % elongation. It's worth noting that each test was repeated at least four times.

To calculate the average diameter of the threads, they were considered as cylindrical in shape, and the following equation was applied:

$$D = \sqrt{\frac{4 \times \left(\frac{m}{\rho}\right)}{L \times \pi}} \quad (5)$$

where, m : is the weight of thread, ρ : is the density and L : is the length.

Micromeritics AccuPyc 1330 gas pycnometer was used to measure the density of flax fabrics. The sample is closed in the instrument compartment of known volume, the inert gas (Ar) is introduced, and

then expanded into another precision internal volume. The pressure before and after expansion is measured and used to calculate the sample volume. Dividing the sample weight into this volume gives the sample density. Weight, density, volume and diameter of threads are listed in (Table S1). This test is adapted from Ferrara's study [49], which have performed a tensile strength test of flax fabrics.

4. Results and discussion

4.1. FTIR and EDS spectroscopies

DVTS, F/pristine, F/pre-treated and F/Si-vinyl were analysed by FTIR spectroscopy to confirm the grafting of flax fabrics with the presence of characteristic bands of vinyl groups (Fig. 3, a). The bands corresponding to the vinyl group (C=C stretching at 1592 cm^{-1} , =C-H bending at 830 cm^{-1}), the Si-CH₃ groups at 1250 cm^{-1} and 780 cm^{-1} and the silazane groups (N-H at 1175 cm^{-1} , Si-N at 925 cm^{-1}) are highlighted in the DVTS spectrum.

F/pristine and F/pre-treated show similar spectra with bands corresponding to the hydroxyl groups (-OH) at 3330 cm^{-1} and the ether group (-C-O-C-) at 1025 cm^{-1} of the cellulose. Concerning the F/Si-vinyl, bands characteristic of the vinyl and Si-CH₃ groups are present on the spectrum while the silazane bands are not observable. The disappearance of the characteristic bands of the SiN-H and Si-NH bonds confirms the consumption of silazane functions due to the reaction with the hydroxyl groups, while the presence of signals of vinyl and Si-CH₃ groups confirms the grafting of the dimethylvinylsiloxane part on the flax fabric surface.

The fibers cross-section of the pristine and modified fabrics was analysed by SEM/EDS to obtain a silicon mapping to confirm the presence of the grafting after DVTS treatment. As it is clearly confirmed in EDS images (Fig. 3b), silicon is naturally present in flax fabric but only in trace amounts. On the other hand, for the fabric treated with alkali, silicon element is almost absent in comparison to F/pristine which was attributed to its elimination by the alkaline solution. Finally, for F/Si-vinyl, silicon is present in abundance and homogeneously distributed on/into fibers (in the whole section). The presence of the silicon element proves the presence of the grafted vinyl groups. These results are

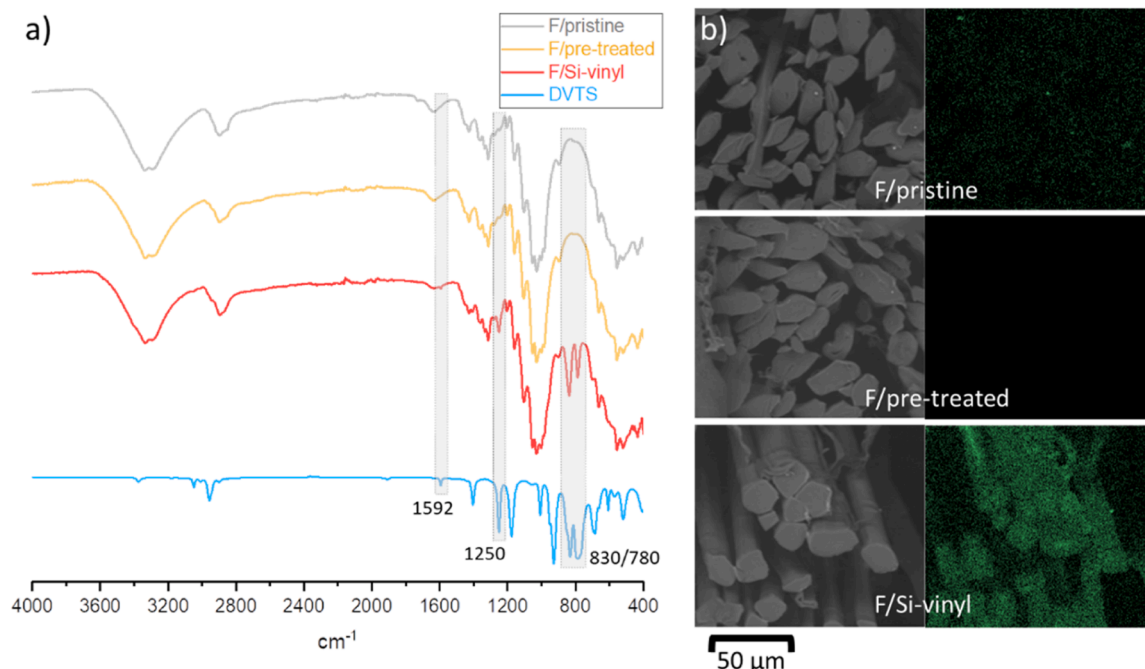


Fig. 3. a) FTIR spectra and b) SEM/EDS images of F/pristine, F/pre-treated and F/Si-vinyl.

consistent with those obtained in previous work [43] and confirm the successful of this functionalization process on the flax fabrics.

PDMS-co-PHMS, and the corresponding grafted flax fabrics F/PDMS-co-PHMS were also analysed by FTIR spectroscopy to confirm the grafting PDMS-co-PHMS (Fig. 4, a). The bands corresponding to Si—H at 2160 cm^{-1} and Si—CH₃ at 1250 cm^{-1} are observable in the PDMS-co-PHMS spectra. In the spectra of grafted fabrics, Si—CH₃ characteristic bands are present with great intensity while the Si—H band is not observed. The disappearance of the characteristic band of the Si—H functions is due to their reaction with the vinyl groups, previously introduced by silazane treatment. The presence of the Si—CH₃ band and the increase in its intensity compared to flax grafted with only vinyl functions, proves the grafting of PDMS-co-PHMS co-polymer.

An observation of the cross-section of the grafted fabrics by SEM/EDS using Silicon mapping confirmed the presence of the grafted PDMS-co-PHMS through the whole section with a great intensity of Silicon (Fig. 4b).

4.2. Determination of silicon content in the grafted fabrics by X-ray fluorescence elemental analysis

F/pristine and modified fabrics were characterized by X-ray fluorescence spectrometry. The Silicon content for each fabric was calculated using equation 4 (Fig. 5).

The silicon content in the F/Si-vinyl and F/PDMS-co-PHMS is about 4.4 and 9.6 wt%, correspond to 13 and 27 wt% of grafting rate (GR) wt% (Eq S1 and Eq S2), respectively, which is the maximum grafting rate for each one. The difference of Silicon content between the two types of grafted fabrics is almost double. The comparison of these results with the (Fig. 1) seems to validate the grafted chains structure.

4.3. Hydrophobicity of grafted flax fabrics

While F/pristine and F/pre-treated fabrics exhibited complete water droplet absorption, F/Si-vinyl displayed relatively good hydrophobic properties, with θ about $132^\circ \pm 3$. However, SA was notably high at around 85° . In contrast, F/PDMS-co-PHMS demonstrated excellent hydrophobicity, allowing water droplets to easily roll on across the fabric surface without causing wetting. These droplets maintained a spherical shape and remained on the fabric surface for over 30 min. θ and SA for this fabric measured approximately $147 \pm 5^\circ$ and $15 \pm 2^\circ$, respectively.

As the silicon materials have low surface energy, the grafting of siloxane compounds decreases the surface energy of the flax fabric exhibiting good hydrophobic properties [50]. Nevertheless, as mentioned above, F/Si-vinyl has displayed hydrophobic properties with a relatively good contact angle θ about (132°), but SA was unfavourable (about 85°) and was not suitable for self-cleaning application. Comparing the hydrophobic properties of F/Si-vinyl and F/PDMS-co-PHMS, there is a small difference in terms of θ but a significant one in terms of SA. Several reasons are suggested to explain this difference: 1/ the amount of Silicon grafted on the fabric is higher for F/PDMS-co-PHMS, or 2/ the type of siloxane compound that is grafted possibly changes in the morphology (roughness) of the fabric surface. To investigate these reasons, other samples of grafted fabrics with different Si content were prepared.

The Table 1 shows the values of θ and SA for F/Si-vinyl and F/PDMS-co-PHMS samples with different Si contents. F/Si-vinyl with 2.3 wt% of Si content has θ and SA about 134° and 84° , respectively. When the Si content increases from 2.3 to 4.4 wt% which represents an increase around 90 %, no change occurs in terms of contact and sliding angles. This means that the content of Si has no effect on the wettability of the modified fabrics.

On the other hand, F/PDMS-co-PHMS with 4.9 wt% of Si content has a bigger θ and much smaller SA compared to those of F/Si-vinyl with very close Si content (4.3 wt%). The difference lies in the type of chemical composition of the silane unit of the grafted compound and its surface tension in each sample. Indeed, in F/PDMS-co-PHMS the silane unit is $((\text{CH}_3)_2\text{SiO})$ while in F/Si-vinyl, the unit is dimethylvinylsiloxane.

Moreover, when the Si content in F/PDMS-co-PHMS increases to 9.6 wt%, the SA decreases to 15° . This can be attributed to the increased area covered by the siloxane chains. However, the change of surface morphology during the grafting process is also a possible reason and needs to be investigated, especially since it is known that there is a clear relationship between surface roughness and wettability [51,52].

A confocal laser scanning microscopy analysis was performed on F/pristine, F/pre-treated, F/Si-vinyl and F/PDMS-co-PHMS in order to investigate the evolution of the surface roughness during the treatment process (Figure S2).

This analysis allows to calculate the Sdr % parameter which provides the developed interfacial area ratio and which can be used to assess the evolution of surface roughness of the flax fabric at the thread level in a range scale between (100–1000 μm).

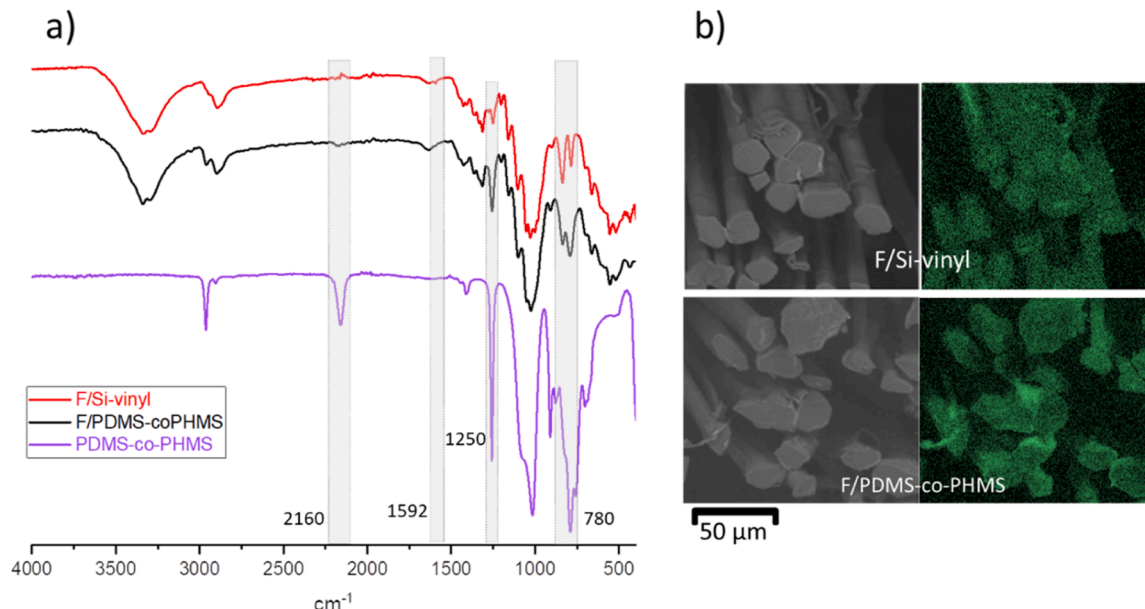


Fig. 4. a) FTIR spectra and b) SEM/EDS images for F/Si-vinyl and F/PDMS-co-PHMS.

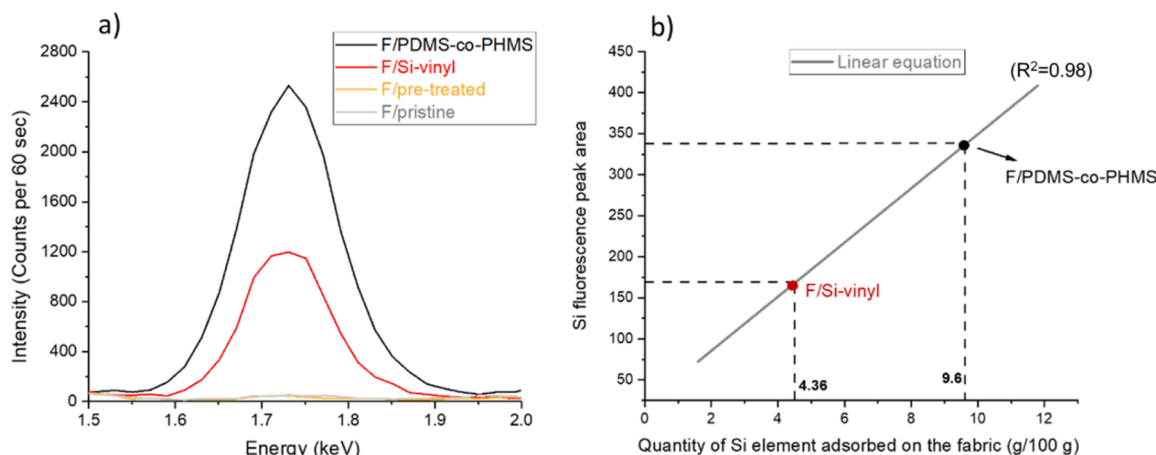


Fig. 5. (a) X-ray fluorescence spectrum of the Silicon band for pristine, F/pre-treated, F/Si-vinyl and F/PDMS-co-PHMS and (b) X-ray fluorescence analysis to determine Silicon concentration in flax fabrics based on a calibration curve carried out with a fabric impregnated with D₄.

Table 1

Contact and sliding angles values for F/Si-vinyl and F/PDMS-co-PHMS samples with different Si content.

Samples	Si content (wt%)	Contact angle (°)	Sliding angle (°)
F/Si-vinyl (I)	2.3	134 ± 2	84 ± 4
F/Si-vinyl	4.3	132 ± 3	85 ± 5
F/PDMS-co-PHMS (I)	4.9	145 ± 4	25 ± 3
F/PDMS-co-PHMS	9.6	147 ± 5	15 ± 2

Sdr% values for F/pristine were between 785 and 1640 while they increased up to 1920–2890 for F/pre-treated (Fig. 6). The pre-treatment step with NaOH solution increased the Sdr% value i.e., the surface roughness. This result is consistent with the literature when flax fibers are treated with an alkaline solution. This type of treatment deforms the stuffed structure of the fiber by the removal of lignin and non-cellulosic materials, resulting to the separation of the fibers from each other and thus improving the surface roughness [53,54]. On the other hand, the range of Sdr % values for F/Si-vinyl has considerably expanded, spanning from 300 to 4270, which can be attributed to the silazane treatment producing an inhomogeneous fibers dispersion. However, this range has not changed for F/PDMS-co-PHMS sample, indicating no change in surface roughness has occurred at least on this scale. Also, SEM micrographs (Figure S3) at the scanning scale of 20–50 μm show no apparent

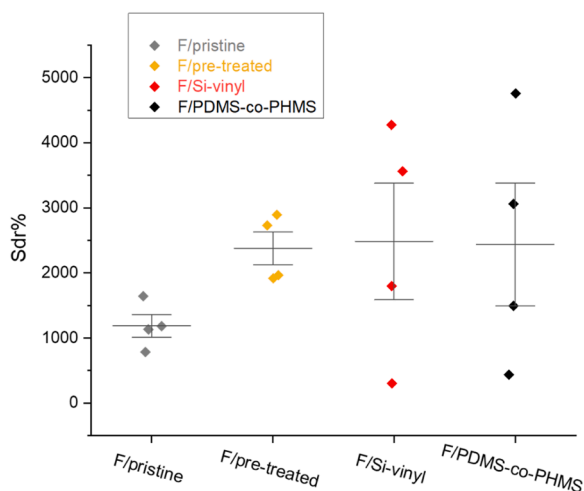


Fig. 6. Sdr % values of F/pristine, F/pre-treated, F/Si-vinyl and F/PDMS-co-PHMS.

difference between the F/pristine, F/pre-treated, F/Si-vinyl and F/PDMS-co-PHMS. Thus, the decrease of SA value cannot be assigned to an increase in surface roughness and may be rather due to the increased area covered by the siloxane chains. A small SA value is needed to allow the rolling of droplets on the fabric surface at small inclination angles [55]. This is a prerequisite for achieving self-cleaning properties.

4.4. Self-cleaning and durability

To verify the self-cleaning ability, a lab-scale method has been designed. Some mud, coffee, and tomato sauce were deposited on F/pristine and F/PDMS-co-PHMS and then cleaned by dropping water over it. As shown in Fig. 7, the contaminants are easily taken away and rolled on the grafted fabric by the moving water droplets, resulting in a completely clean surface while the contaminants on F/pristine fabric are difficult to clean in a similar way, they left clear stains on the fabric surface after dropping water over it. This indicates the efficacy of F/PDMS-co-PHMS on the self-cleaning property. Videos S1 and S2 in supporting information show the effectiveness of this fabric treatment for water repellence.

In order to show the potential durability, the grafted fabrics have been tested with two tests, acid solution washing and home wash. The durability of hydrophobic grafted fabrics has been investigated using a lab-simulation of a home wash. The X-ray fluorescence elemental analysis was used to follow the decrease of Silicon concentration in the grafted fabrics due to the removal of PDMS derivatives molecules during the washing cycles. The durability tests were performed on F/PDMS-co-PHMS. The quantity of silicon element slightly decreased during the first 3 washing cycles with a loss of about 16 % of the total Silicon content (Figure S4). It remained almost stable during the next 7 washing cycles with a negligible loss (about 3 %) without any change neither in wettability properties, according to the contact angles measurements ($146 \pm 2^\circ$ after washing vs $147 \pm 5^\circ$ before washing) nor in morphology. That means the washing has only a slightly effect on the Silicon content in the grafted fabric. Moreover, this effect becomes less significant after the first washing cycles, which demonstrates the washing resistance.

Furthermore, F/PDMS-co-PHMS has displayed a highly resistance to the acid medium. After immersing the samples 3 h at room temperature in HCl solution of pH = 2, the Si loss was only about 2.7 % of the total silicon content. Thus, the Si content has almost not changed, confirming the high chemical stability of grafted chains on the flax fabric.

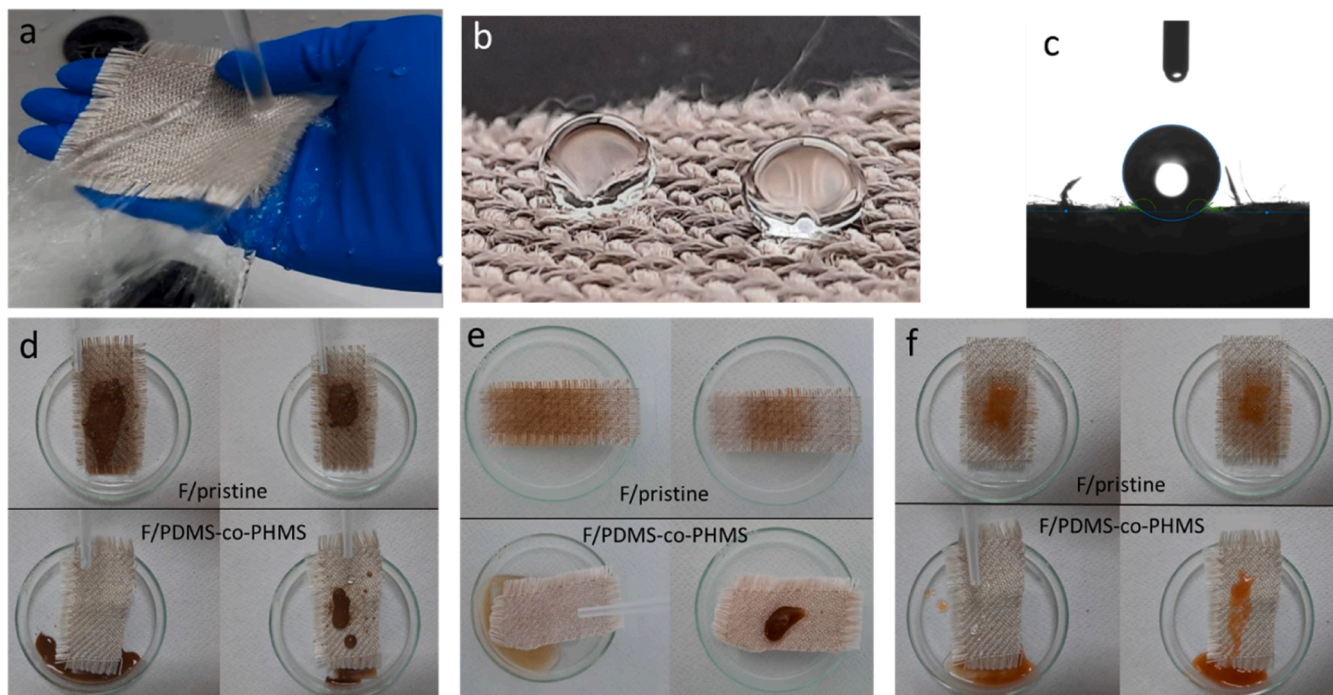


Fig. 7. Hydrophobicity of F/PDMS-co-PHMS a) Sliding of flowing water over the fabric surface. b) Standing of water droplets on the fabric surface with spherical shape. c) Contact angle measurement for water. d, e, f) Self-cleaning performances with mud, coffee, and tomato.

4.5. Mechanical properties

Tensile test was performed on threads of F/pristine, F/pre-treated and F/PDMS-co-PHMS in order to investigate the evolution of mechanical behaviour of flax fabric before and after grafting process.

Stress strain curves of pristine, pre-treated and PDMS-co-PHMS grafted threads (Figure S5 and S6) display the change occurring on mechanical properties. The values of maximum tensile force stress (F_{max}), elongation at maximum force ($dL(F_{max})$) and Young modulus (E) obtained by tensile test are listed in Table S2.

Values of Young modulus are about 20.0 ± 1.1 , 7.8 ± 0.8 and 7.8 ± 0.5 GPa for pristine, pre-treated and PDMS-co-PHMS grafted threads, respectively. Young modulus decreased about 60 % due to the removal of lignin by the pre-treatment with NaOH. Indeed, lignin typically has highly cross-linked and branched structures that play an important role in maintaining the proper orientation cellulose fibers. Consequently, they contribute significantly to the structural straightness and rigidity of the cellulose fibers. Consequently, the elimination of this component from the fiber would result in a reduction in the fiber's Young's Modulus [56]. However, this step is very important for the success of the grafting process. In our previous work [36] it was shown that the lignin removal induced silazane diffusion into the fiber. Also, Valadez-Gonzalez et al. have shown that this step is necessary to facilitate the diffusion of the coupling agents inside the fibers [57].

In contrast, pre-treated and PDMS-co-PHMS grafted threads have the same Young modulus. Thus, the grafted molecules onto the flax fabric do not impact the stiffness.

Furthermore, it's noteworthy that the maximum force (F_{max}) exhibited by the pristine thread significantly exceeds that of both the pre-treated and PDMS-co-PHMS grafted threads. This observation underlines the impact of these treatments on the thread's mechanical properties. While the elongation at maximum force ($dL(F_{max})\%$), remained nearly consistent for all three samples: F/pristine, F/pre-treated, and F/PDMS-co-PHMS. Thus, there is no significant difference in terms of tensile elongation among them, suggesting that the treatments have a more pronounced influence on the maximum force capacity rather than the extent of elongation at this point.

5. Conclusions

Flax fabrics have been first functionalized with vinyl groups using DVTS and then with PDMS-co-PHMS via a hydrosilylation reaction in the presence of Karstedt catalyst.

The successful integration of silicon element into the entire flax fiber structure was confirmed through silicon mapping, which displayed a uniform distribution of the grafted compound with a notably high intensity.

The type of chemical composition of the silane unit of the grafted compound and the extent of coverage by the siloxane chains have a great impact on the contact and sliding angles.

The confocal laser scanning microscopy analysis allowed for the investigation of fabric surface evolution by measuring the Sdr % value. This analysis showed that the treatment of flax fabric with DVTS resulted in a fiber dispersion similar to that achieved with the PDMS-co-PHMS treatment.

In terms of durability and resistance, the grafted flax fabrics exhibited an interesting potential stability even after repeated washing cycles and exposure to acidic environments. In order to have a deeper insight of the grafted fabrics durability it would be interesting in the next study to perform an abrasion test, a wear test or an alkali wash resistance test.

However, it should be noted that the pre-treatment of flax fabric with NaOH, which is necessary to facilitate the interaction with DVTS, leads to some reduction in the fabric's mechanical properties. Despite this drawback, the enhancement of hydrophobicity, and durability makes the F/PDMS-co-PHMS-treated flax fabric a promising candidate for self-cleaning applications.

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CRediT authorship contribution statement

Antoine Ishak: Writing – original draft, Methodology, Investigation, Formal analysis. **Rodolphe Sonnier:** Writing – review & editing, Conceptualization, Validation, Supervision, Project administration, Funding acquisition. **Belkacem Otazaghine:** Writing – review & editing, Conceptualization, Funding acquisition, Supervision. **Hélène Garay:** Formal analysis. **Claire Longuet:** Writing – review & editing, Validation, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Supplementary materials

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