



Facing the rain after the phase out: Performance evaluation of alternative fluorinated and non-fluorinated durable water repellents for outdoor fabrics

S. Schellenberger ^{a,*}, P. Gillgard ^b, A. Stare ^b, A. Hanning ^b, O. Levenstam ^c, S. Roos ^b, I.T. Cousins ^a

^a Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, Sweden

^b Swerea IVF AB, Mölndal, Sweden

^c Swedish School of Textiles, University of Borås, Sweden

HIGHLIGHTS

- Chemical alternatives assessment of presently available durable water repellents (DWRs).
- Focus on functionality as first criteria for selecting chemical alternatives.
- Evaluation of textile repellency with fluorinated and non-fluorinated DWRs.
- Durability test as basis for a comparative life-cycle assessment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 9 September 2017

Received in revised form

5 November 2017

Accepted 6 November 2017

Available online 7 November 2017

Handling Editor: J. de Boer

Keywords:

Chemical alternatives assessment
Per- and polyfluoroalkyl substances outdoor apparel
Water repellency
Oil repellency
Sustainability

ABSTRACT

Fluorinated durable water repellent (DWR) agents are used to obtain water and stain repellent textiles. Due to the on-going phase-out of DWRs based on side-chain fluorinated polymers (SFP) with “long” perfluoroalkyl chains, the textile industry lacks suitable alternatives with comparable material characteristics. The constant development and optimization of SFPs for textile applications initiated more than half a century ago has resulted in a robust and very efficient DWR-technology and textiles with exceptional hydro- and oleo-phobic properties. The industry is now in the predicament that the long-chain SFPs with the best technical performance have undesirable toxicological and environmental behaviour. This study provides a comprehensive overview of the technical performance of presently available fluorinated and non-fluorinated DWRs as part of a chemical alternatives assessment (CAA). The results are based on a study with synthetic outdoor fabrics treated with alternative DWRs and tested for repellency using industrial standard and complementary methods. Using this approach, the complex structure-property relationships of DWR-polymers could be explained on a molecular level. Both short-chain SFPs and non-fluorinated DWRs showed excellent water repellency and durability in some cases while short-chain SFPs were the more robust of the alternatives to long-chain SFPs. A strong decline in oil repellency and durability with perfluoroalkyl chain length was shown for SFP DWRs. Non-fluorinated

* Corresponding author. Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, Svante Arrhenius väg 8, SE-114 18, Stockholm, Sweden.

E-mail address: steffen.schellenberger@aces.su.se (S. Schellenberger).

alternatives were unable to repel oil, which might limit their potential for substitution in textile application that require repellency towards non-polar liquids.

© 2017 Published by Elsevier Ltd.

1. Introduction

The regulation and growing consumer awareness of harmful chemicals in textiles (Sherburne and Blackburn, 2009) has led to a trend towards the use of more sustainable materials in textile production (Shahid-ul and Mohammad, 2014; Shahid ul et al., 2013). This paradigm shift from the traditional approach of producing textiles with highest material efficiency at lowest costs, to one that assigns economic value in eliminating emissions of hazardous chemicals, can for example be seen in the large textile segment of “functional textiles”. Functional textiles in contrast to e.g. fashion clothing, above all are designed to contain certain technical functions. Outdoor, sports and personal protective garments are based on functional textiles. Nevertheless, textile function can also be associated with fashion since “branding” (Ruckman, 2005) and the desire to “wear what the experts wear” is likely to influence consumers purchasing behaviour. One key functionality of those textiles in general is to provide weather protection and body moisture management to the wearer (Song, 2011; Hu, 2016; Mukhopadhyay and Midha, 2008; Weder, 1997; Tanner, 1979). These functionalities can be achieved for example with a multi-layered fabric construction (Fig. 1 a1), in which a liquid-repelling outer fabric is combined with a waterproof membrane on the inside. The repellency of the outer fabric is achieved with liquid repelling hydrophobic polymers (Holmquist et al., 2016). These “durable water repellents” (DWRs) form a continuous polymer film around each fibre of the outer fabric which delays liquid penetration of e.g. rain droplets (0.02–0.3 mm in diameter). Because of the porosity of the materials used in multi-layered fabric construction, the textile remains water vapour permeable and enables the transport of moisture droplets (usually <0.4 nm diameter (Hu, 2016)) from the inside to the outside, as shown in Fig. 1 a2. In some applications textile repellency to non-polar liquids is essential. One example is for workwear used in

chemical plants, in which the DWR coating is a lifesaving protection as well as providing the necessary water (and other liquid) repellence. An insufficient DWR treatment can cause a complete wetting (“wet-out”, Fig. 1 a4) of the woven fabrics due to transport of water into the fibrous assembly caused by capillary forces or external forces like high hydrostatic pressure (Kissa, 1996) (e.g. due to the high kinetic energy of rain droplets in a cloud burst). Complete wetting of the fabrics can cause significant cooling of the wearer and can, under extreme weather conditions, be life threatening.

Functional textiles based on DWR surface modifications (Pan and Sun, 2011) of natural and synthetic fibres have resulted in products of ever-increasing popularity for more than half a century. The most effective DWRs used in this application since the late 1950s (Ahlbrecht et al., 1957) are based on side-chain fluorinated polymers with long perfluoroalkyl side chains: C_nF_{2n+1} and $n \geq 7$, in this study referred to as L-SFPs (Fig. 1 b). Fluorinated polymers in general were originally developed for space missions (Kleiman and Tennyson, 2012) and have revolutionized the functional textile market (McCann, 2005) due to their high stability and exceptional material characteristics (Holmquist et al., 2016; Krafft and Riess, 2015).

The perfluoroalkyl moieties in these L-SFPs, which are both water (hydrophobic) and oil (oleophobic) resistant (Fig. 1 b), are linked via flexible molecule segments called spacers (S in Fig. 1 b) to a “carrier polymer” (P in Fig. 1 b) that forms a film around the fibres. These polymers ensure the durability of the water and oil repellency during chemical and mechanical stress (e.g. washing, weathering and abrasions). Acrylates, polyurethanes and particles made of hyperbranched polymers (Tang et al., 2010) or nanoparticles (Zhang et al., 2003) denote typical carrier polymer systems. Due to the flexibility of the spacer, the repellent perfluoroalkyl moieties are able to self-assemble into a crystallized (Honda et al., 2005), hydrophobic shell around the fibre.

The main physicochemical explanation of a DWR-treated

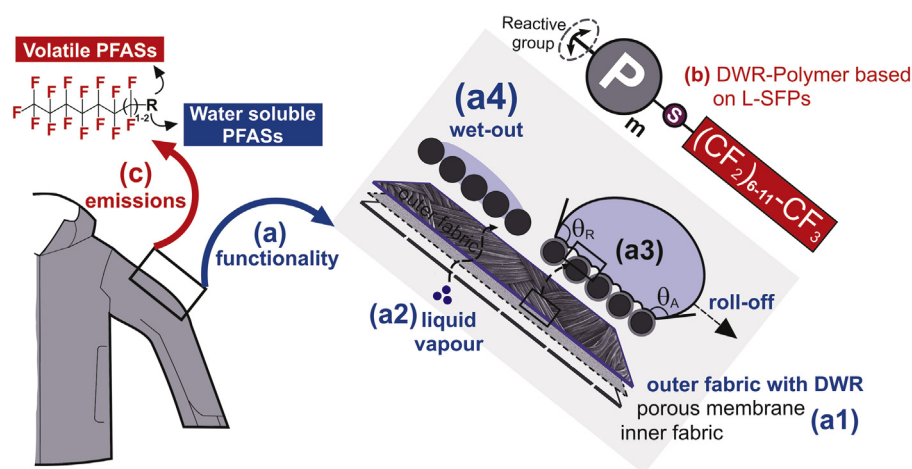


Fig. 1. Schematic representation of the functionality (a) of performance outdoor textiles that are based on a layered fabric construction (a1) that allows both breathability (a2) and provides a liquid barrier (a3) for droplets from the outside. This is enabled by a combination of a water vapour permeable membrane and an outer fabric that is treated with a water and oil repelling DWR polymer (b) based on L-SFPs. L-SFPs consist of a perfluoroalkyl moiety linked to a spacer (S) and further to a polymer backbone (P). This allows the formation of a durable cross-linked film around single fibres. L-SFPs on textiles give rise to the emission of PFOA, PFOS and other kinds of PFASs (c).

textile's repellency can be expressed by the modified Young Equation for rough surfaces as described by [Wenzel \(1949\)](#).

$$\cos\theta' = r \frac{(\gamma_{SG} - \gamma_{SL})}{\gamma_{LV}}$$

Due to the combination of hydrophobic fibres and a rough surface of fibrous assemblies, water droplets minimize their contact area (and surface free energy ([Owens and Wendt, 1969](#))) to the textile surface resulting in the “Lotus-like” Cassie-Baxter wetting ([Blossey, 2003](#)) (above) with air trapped below the drop. This causes a very low adhesion and liquid droplets are easily repelled without leaving water films between the fibres (see [Fig. 1 a3](#)). Thus the contact angle θ' of a liquid droplet on a textile surface is a consequence of surface roughness (r ; roughness may facilitate repellency further) of the weave and the three interfacial tensions γ_{SV} (surface energy of the fibre surface); γ_{SL} (interfacial tension of the liquid droplet that is in contact with the fibre surface) and γ_{LV} (surface tension of the liquid). In order for a textile surface to repel different kinds of liquids, e.g. polar liquids like water or coffee, or non-polar liquids like sun lotion or olive oil, the surface energy of the fibre surface (γ_{SV}) needs to be lower than the surface tension of the liquid (γ_{LV}) ([Bernett and Zisman, 1959](#)). Since the surface energy of the crystallized perfluoroalkyl chains is extremely low (ranging typically from γ_{SG} 6–11 mN/m for an ideal crystallization of CF_3 -groups ([Shafrin and Zisman, 1959](#))), textiles with L-SFPs are able to repel both polar (e.g. water) and non-polar liquids (e.g. oils). This is critically important functionality for industrial protective clothing ([Mansdorf and Sager, 1988](#)), but also reduces the staining tendency in outdoor clothing ([Rao and Baker, 1994](#)).

Although L-SFPs have useful properties for industrial and consumer applications, they have also been shown to diffusely emit long-chain perfluoroalkyl and polyfluoroalkyl substances (PFASs) (see [Fig. 1c](#)). Of particular concern is the release of persistent, bio-accumulative and toxic long-chain perfluoroalkyl acids (PFAAs) into the environment ([van der Veen et al., 2016](#); [Berger and Herzke, 2006](#); [Knepper et al., 2014](#)). The release of PFAAs occurs either through the direct release of residual PFAAs (“direct” sources) from textiles or through the release and subsequent degradation of so-called “precursor” substances from textiles, which transform to PFAAs in the environment (“indirect” sources). Precursors can be relatively low molecular weight molecules present as residuals in the textiles such as the volatile fluorotelomer alcohols ([Ellis et al., 2004](#)) (FTOHs) or high molecular weight substances such as the DWR polymers themselves ([Li et al., 2017](#)). For example, the polymeric structure of L-SFPs can potentially degrade in the environment via hydrolysis into perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) as the most prominent examples of molecules generated from precursor degradation. Concerns over the risks associated with long-chain PFAAs has led to their recent phase-out and regulation ([EPA, 2006](#); [Renner et al., 2005](#)) and thus L-SFPs are currently only used in few textile applications (e.g. in the military).

Modern DWRs are either based on polymers with short perfluoroalkyl side chains of the type C_nF_{2n+1} , $n \leq 6$ (in this work referred to as s-SFPs) or based on fluorine free materials. S-SFPs still utilize the structural principles of the L-SFPs as described before. There is also a growing number of non-fluorinated DWR-products on the market, often advertised with assurances of good technical performance and benign environmental fate. Polydimethylsiloxanes (Sis) and hydrocarbons (HCs) are two large groups of non-fluorinated DWR technologies ([Holmquist et al., 2016](#)). The textile industry now faces the dilemma that this substitution took place before the non-fluorinated alternatives were sufficiently characterized for health effects, environmental impacts

([Holmquist, 2016](#)) and technical performance under various conditions.

The durability of the textile's water and oil repellency is an important aspect that can help reduce emissions. Maintaining material properties of the garment after washing, weathering and abrasions implies that sufficient amounts of the DWR molecules remain bound to the fabrics and have not been lost e.g. to the environment. Maintaining the functionality of garments for longer also means the textile's technical lifespan increases, which reduces the emissions of chemicals during production. L-SFPs are known to provide long-lasting oil and water repellency to textiles, but the durability of s-SFP and fluorine free DWRs is unknown.

The main objective of this study is to provide an overview of the technical performance and durability of currently available fluorinated and non-fluorinated DWR technologies for textiles. To the best of our knowledge there are no such detailed studies published that include repellency and durability of alternative DWRs and connect the results found to structure-property relationships on a molecular scale for the DWR-polymers. This research is part of a chemical alternatives assessment (CAA) ([Lavoie et al., 2010](#)) to manage chemical risks associated with L-SFPs being undertaken as part of the SUPFES project (Substitution of Prioritised Poly- and Perfluorinated Chemicals to Eliminate Diffuse Sources). In conducting an CAA, we follow previous recommendations to first focus on considerations of function ([Tickner et al., 2015](#)) in selecting chemicals alternatives. The aim of the SUPFES project, a consortium of scientific and industrial partners, is to help industry find alternatives that can replace the prioritised long-chain fluorinated chemicals which are harmful to the environment. This is achieved by assessing the technical performance and environmental impact from the long-chain fluorinated chemicals and their alternatives.

2. Materials and methods

2.1. Materials

Polyamide (PA) and polyester (PES) fabrics (see [Table S2](#) in the Supplementary material (SM) for detailed specifications) suitable for the production of performance outdoor clothing were provided by FOV AB (Sweden). The fabrics were pre-prepared (washed, subjected to thermal fixation at 190 °C for fabric stabilization, dyed and dried) for the wet treatment process with the different DWR-emulsions.

Aqueous dispersions of DWR polymers, extenders, cross-linkers and catalysts were chosen according to an extensive selection process (see [Figure S1](#)) and kindly provided by different major raw material suppliers.

DWR technologies evaluated in this study were grouped according to the general molecular structure of the moiety which provides the water and oil repellent function and according to their expected environmental fate as reported by [Holmquist et al. \(2016\)](#). Thus DWRs were grouped independent of their polymer backbone or other components in the formulation into fluorinated **SFPs**, and non-fluorinated **Sis** and **HCs** (see [Table 2](#)). Alternative-DWR formulations were compared in practical experiments to a C8 L-SFP reference (phased out raw material). Detailed information about the fibres and DWR formulations are provided in the [SM](#).

2.2. Selection of raw materials

Fabric types used in this study were identified in a survey ([Jönsson, 2014](#)) of 50 textile producing companies conducted by SUPFES to be the most relevant materials for performance outdoor

Table 1

DWRs formulations (see Table S2 for more detailed information).

Fluorinated DWRs		Non-fluorinated DWRs			
FC8-ref	C8-based L-SFP	Si-1	Silicone (Encapsulated)	HC-1	Paraffin wax (Encapsulated)
FC6-1	C6-based s-SFP	Si-2	Silicone	HC-2	Finish based on botanical extracts
FC6-2	C6-based s-SFP based and a hyperbranched polymer	Si-3	Silicone	HC-3	Paraffin wax
FC6-3	C6-based s-SFP	Si-4	Silicone functionalized Polyurethane	HC-4	Hyperbranched polymer with HC-modification
FC4-1	C4-based s-SFP				

Table 2

Spray rating explanations.

ISO 5	ISO 4	ISO 3	ISO 2	ISO 1
No sticking or wetting of the upper surface	Slight random sticking or wetting of the upper surface	Wetting of upper surface at spray points	Partial wetting of whole upper surface	Complete wetting of whole upper surface

clothing used in the consumer market. Since the repellency and durability over the garment's lifetime strongly depends on the choice of DWR-formulation, curing conditions (Schindler and Hauser, 2004) and on industrial expertise, the SUPFES approach has been to work closely with major raw material suppliers. This collaboration has made it possible to apply the DWR-polymers in a laboratory scale in a way that was similar to those used in the textile producing industry under industrial conditions (see Figure S1 in the SM for additional information to the selection process).

2.3. Preparation of DWR formulations

A 1 L volume of each of the DWR formulations was prepared by mixing the different components by using a polytetrafluoroethylene (PTFE)-stirring magnet in a 2 L glass beaker for 5 min at 400 rpm, to ensure a good homogeneity. The stability of the formulations was assessed by visual inspection before application to the fabric.

2.4. Preparation of repellent fabrics

A total of 360 samples of fabrics were prepared and provided the basis for this study. Water-based emulsions of DWRs were applied in a laboratory non-continuous dip coating process (padding), as follows. A piece of fabric (0.14 m²) was immersed in a 2 L glass beaker, containing 1 L of DWR formulation and kept there for 30 s while stirring with a PTFE-stirring magnet. The excess liquid was removed by using a not continuous foulard equipment (device for textile treatment with two rollers; model BVHP, Roaches England) using two runs at 2.9 rpm and a nip pressure of 3.7 bar. After adsorption of DWR polymers to the fibres, the fabrics were dried followed by a curing step in an oven (Discontinuous Labdryer; type LTE; Mathis, Switzerland) to promote the crosslinking reaction of the DWR-polymer (Kissa, 2001) (additional information sample preparations can be found in Table S2).

2.5. Standardised repellency tests

The ISO 4920 ISO, 2012 water repellency spray test method was used to evaluate fabrics' repellency (6 replicates). The test samples were conditioned at 20 ± 2 °C and 65 ± 2% relative humidity (RH). Fabrics containing different DWR treatments (18 × 18 cm) were stretched tight in an embroidery hoop, placed and held at a 45° angle 150 mm under a specified spray head. A volume of 250 ml of water was used for rinsing the fabric. The pattern of the water remaining drops on the fabric's surface was visually judged

according to standardised spray test ratings (see scale in Table 2). The spray rating was modified by allowing intermediate values (1.5, 2.5, etc.) for borderline cases.

The ISO 14419 ISO, 2010 oil repellency test was used to evaluate the fabric's resistance (6 replicates) towards oil penetration (20 ± 2 °C and 65 ± 2% RH). Droplets of 8 different alkanes with different surface tensions (see Table S3) were placed on the fabrics and the wetting behaviour on a 0–8 scale judged after 30 ± 2 s according to the transition from the Cassie-Baxter state (Cassie and Baxter, 1944) (see Figure S4 (A) in the SM) to where complete wetting (wicking) starts to occur (see Figure S4 (B–D) in the SM).

As can be seen in Figure S4 A, good oil repellency is defined by a “shiny” appearance of droplets with a high contact angle (CA). In this state, oil droplets have a low liquid-textile contact area, trap air pockets underneath them and cause a double reflection on the textile-oil interface. A reduced oil repellency occurs when the liquid droplets start reducing their CA (Figure S4 B) and partial wicking occurs, which results in a loss of “sparkle”. During the progressive wetting process, complete wetting (wicking) starts to take place (Fig. 4 B) and oil droplets start to migrate into the capillaries (Figure S4 C) until complete wet-out occurs (Figure S4 D). A failure in oil repellence occurs when after 30 s three of five oil droplets of the same surface tension (γ_{LV}) show a complete wetting (according to Figure S4 C and D). A pass occurs if three (or more) out of four droplets of the same γ_{LV} show a wetting behaviour according to Figure S4 A, which is expressed in a the rating 1–8 (see Table S4). A borderline case occurs if three (or more) of five oil droplets show a wetting behaviour according to Figure S4 B, which is expressed by subtraction of 0.5 for the oil rating that showed the borderline case.

2.6. Other repellency tests

To outline the differences in the technical performance, the industrial standard for water (ISO 4920, ISO, 2012) and oil repellency (ISO 14419, ISO, 2010) were combined with water weight increase (as suggested by Davies, 2014) and contact angle measurements (CA) (Kissa, 1996).

A DSA-30 drop-shape analyser (Krüss GmbH, Germany) was used in combination with an Eppendorf pipette for manually dispensing the droplets (droplet volume = 30 µl). A polynomial fitting algorithm (software option Tangente 2) was used to calculate the CA from the droplet shapes (manual baseline detection).

2.7. Durability tests including washing, abrasion and exposure to artificial weathering

The ISO 26330 ISO, 2001 test method was used to simulate

domestic washing of the fabric. DWR-treated fabrics were washed separately at 40 °C (washing machine: Electrolux; Wascator FDM 71 MP-Lab using Detergent ECE A and PES ballast) to avoid cross contamination, followed by tumble drying (60 °C for 30 min). Water and oil repellency were tested after 1, 2, 5 and 10 washing cycles. Some DWR-treated fabrics were placed in an oven at 100 °C for 10 min to investigate the reorientation behaviour of the hydrophobic side chains. The ISO 12947-2 (ISO, 2016) Martindale test method (NU Martindale; James Heal; UK) was used to test the abrasion resistance of the DWR-treated fabrics by rubbing the fabrics in a Lissajous pattern against standard wool (James Heal). The ISO 4892-3 test method was used to simulate the exposure of DWR-treated fabrics to UV radiation, heat and water to reproduce the weathering effects in actual end-use environment. Fabrics were placed in a Weather-Ometer (Atlas; Atlas Ci 3000; USA) that applied heat, moisture and ultraviolet-light at different intensities (see Table S4 in the SM).

3. Results

3.1. Water repellency

The following section summarizes the main findings of the technical performance evaluation of the state-of-the-art DWRs on PES fabrics. Fig. 2 provides an overview of the initial water repellency of different DWR-types after their application on PES fabrics. The repellency tests with PA fabrics using DWR-types showed an overall comparable performance profile to PES fabrics (results for PA fabrics are summarized in Figure S6 in the SM).

The results of water repellency measurements on PES (Fig. 2a and b) showed good initial spray ratings for most of the L- and s-SFP-treated fabrics, although FC6-3 performed less favourably than

other SFP-based DWRs for an unknown reason. The more precise analysis of the weight increase from water absorbed into the fabric after the spray test showed the lowest amount of remaining water on the fabric for the C8-based L-SFP. C4 to C6 based s-SFPs with high spray ratings retained slightly more water on the fabrics, indicating a lower resistance to surface wetting. SFPs with high spray ratings also had higher CA values for water in comparison to all other non-fluorinated DWRs. The best SFP-based DWRs had CAs of $>148^\circ$, which is near to the superhydrophobic state defined in literature (Wang and Jiang, 2007) ($CA > 150^\circ$). Moreover, Fig. 2 illustrates that the initial water repellency of the fluorine free DWR alternatives grouped under silicon (Sis) and hydrocarbon (HCs) is dependent on the choice of specific formulations. The differences in spray rating within the group of Sis were high. Although Si-2 showed a high spray rating (4.7) with a low increase in water weight, fabrics treated with Si-3 showed an inferior performance. The HC-DWRs in general showed slightly lower deviation in the spray test compared with the Sis. Some DWR-formulations obtained satisfying water repellency (i.e. initial spray rating >3) while others did not perform satisfactorily to make them realistic alternatives to L-SFP-DWRs.

It was shown that the complementary repellency measurements used in this study (weight increase of absorbed water and CAs) provided good correlations to the industrial spray test ratings (Figure S7 in the SM displays the Pearson correlation between the different water repellency measurements for PES and PA). The results from the spray test and the absorbed water for PA and PES fabrics showed a strong negative correlation (see $R_{PES} = -0.79$ in Figure S7 a1 and $R_{PA} = -0.83$ in Figure S7b). It was further encouraging that there were strong positive correlations between CA (CA_{H_2O}) measurements and water absorption ($R_{PES} = -0.77$ Figure S7a2) and spray ratings and CAs ($R_{PES} = 0.78$ Figure S7b) for

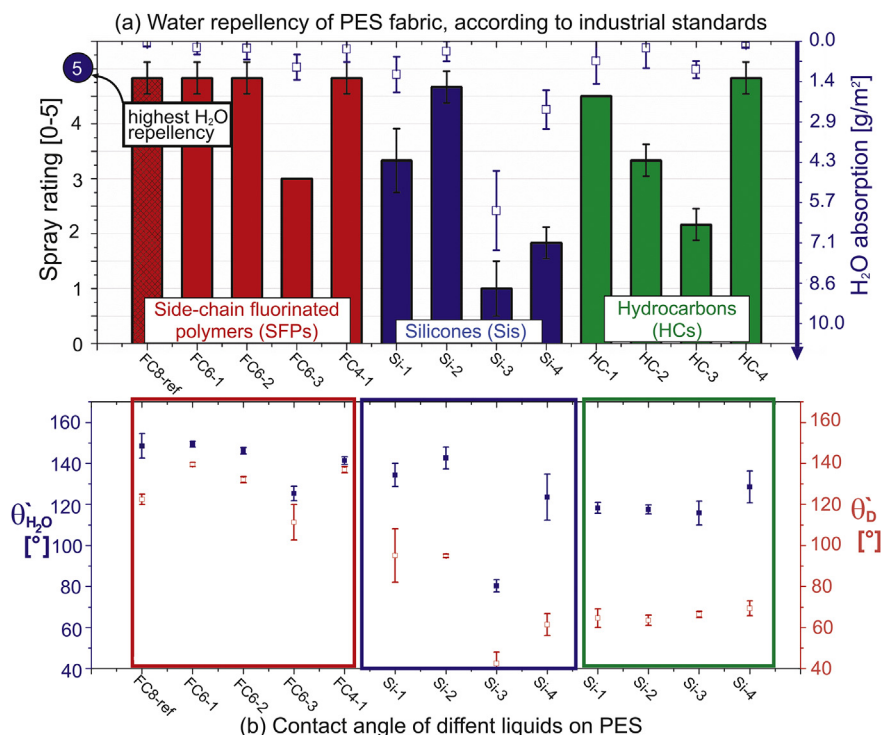


Fig. 2. Liquid repellency measurements for PES fabrics treated with different DWR-types using (a) the industrial test standard ISO 4920 to determine the water repellency (spray rating, primary scale, bars with error bars showing the standard deviation of $n = 6$ measurements) in combinations with measuring the absorbed water (H_2O Absorption [g/m²]; inverse secondary scale, squares with error bars showing the standard deviation of $n = 6$ measurements), (b) contact angles of water (α_w) and diiodomethane (α_d) on the same fabrics (with error bars showing the standard deviation of $n = 6$ measurements.). The different DWRs tested (FC8-ref, FC6 etc.) are specified in Table 1 and Table S2 in the SM.

PES. However, for high spray ratings and low water absorption, the water repellency measurements could not always be explained with CA measurements (e.g. for a spray rating 5 and a water absorption close to 0, the CA measurements varied between 115° and 154°).

3.2. Oil repellency

As can be seen in Fig. 3, the oil repellency on PA and PES strongly depends on the DWR-chemistry used for the fabric treatments. Although the best performing DWR-types were chosen to illustrate the results, only fluorinated materials showed resistance towards wetting by oils. The oil repellency was more sensitive than water repellency towards changes in perfluoroalkyl chain length (see Fig. 3 a1). Only the C8 based L-SFPs ($R-C_8F_{17}$) achieved a very high oil repellency while the values were reduced as the chain length was shortened. All Si and HC compounds showed an oil rating of 0, but still provided some repellency compared to untreated fabrics (see Fig. 3 b3).

3.3. Durability

Durability is another important parameter that has to be considered when assessing the technical performance of different DWRs. Garments undergo wear and tear during use, which causes a reduction in their repellency. Washing (exposure to heat, mechanical forces, detergents, other chemicals and pH 9–11) (Zimmermann et al., 2013), mechanical stress in the form of abrasion and weathering (UV-light, humidity and microbial stress) were identified as the most important factors that might cause wear of the DWR coating and gradually decrease hydro- and oleo-phobicity. Fig. 4 summarizes the selected results of the durability tests for the best performing DWRs in each class (detailed results for all DWRs

can be found in Figure S8–S15 in the SM).

The spray rating (water repellency) after applying the different durability tests showed the highest possible spray rating (5) for the C8 L-SFPs. Decreasing water repellency was observed with decreasing perfluoroalkyl chain length when comparing all durability parameters. This trend was especially visible for the C4 s-SFP that had good initial spray rating, but showed a reduced water repellency after abrasion and weathering. Good durability results were also obtained for the best non-fluorinated DWRs. While fabrics that were treated with Si-DWRs had acceptable spray ratings for water repellency after durability tests, the non-fluorinated HC-DWR showed excellent spray ratings for water repellency that were comparable to the best fluorinated s-SFPs after durability tests. Non-fluorinated DWRs showed no oil repellency before or after washing. For the fluorinated SFPs, it is clear that oil repellency is very much decreased after washing. The C8 L-SFP showed a strong drop in oil repellency after washing and for C4 s-SFPs oil repellency was almost entirely lost.

Another part of the experimental work included heat treating fabrics at a relatively high temperature (100 °C for 10min) and re-performing the spray test with water. This experiment was done for DWR-samples that had a strong reduction in water repellency after 5/10 washing cycles (see Fig. 5). It can be concluded from these results that heat applied during tumble drying after washing (60 °C/30min; which was in agreement with the recommendations usually given by brands of performance outdoor clothing garments (Burman, 2014)) would not be sufficient to restore the water repellency after several washes.

4. Discussion

A good liquid repellency in a fabric is achieved by densely packed hydrophobic moieties (see Fig. 3 a1 and 5) that point

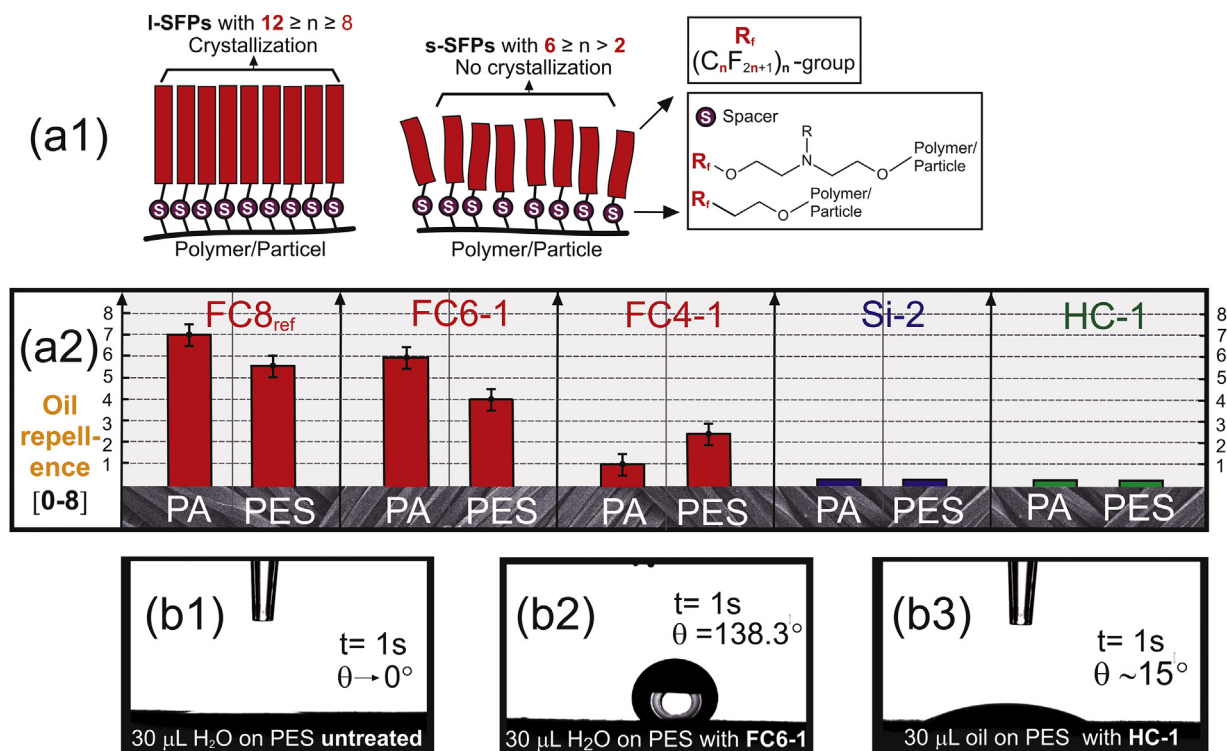


Fig. 3. Schematic representation of the (a1) side chain orientation of SFPs and the measurement of (a2) the resulting oil repellency and different wetting behaviours of mineral oil with (b1) no liquid resistance of the non-treated PES, (b2) superoleophobic repellency with the C8-based I-SFP and (b3) poor oil resistance using a hydrocarbon-based DWR.

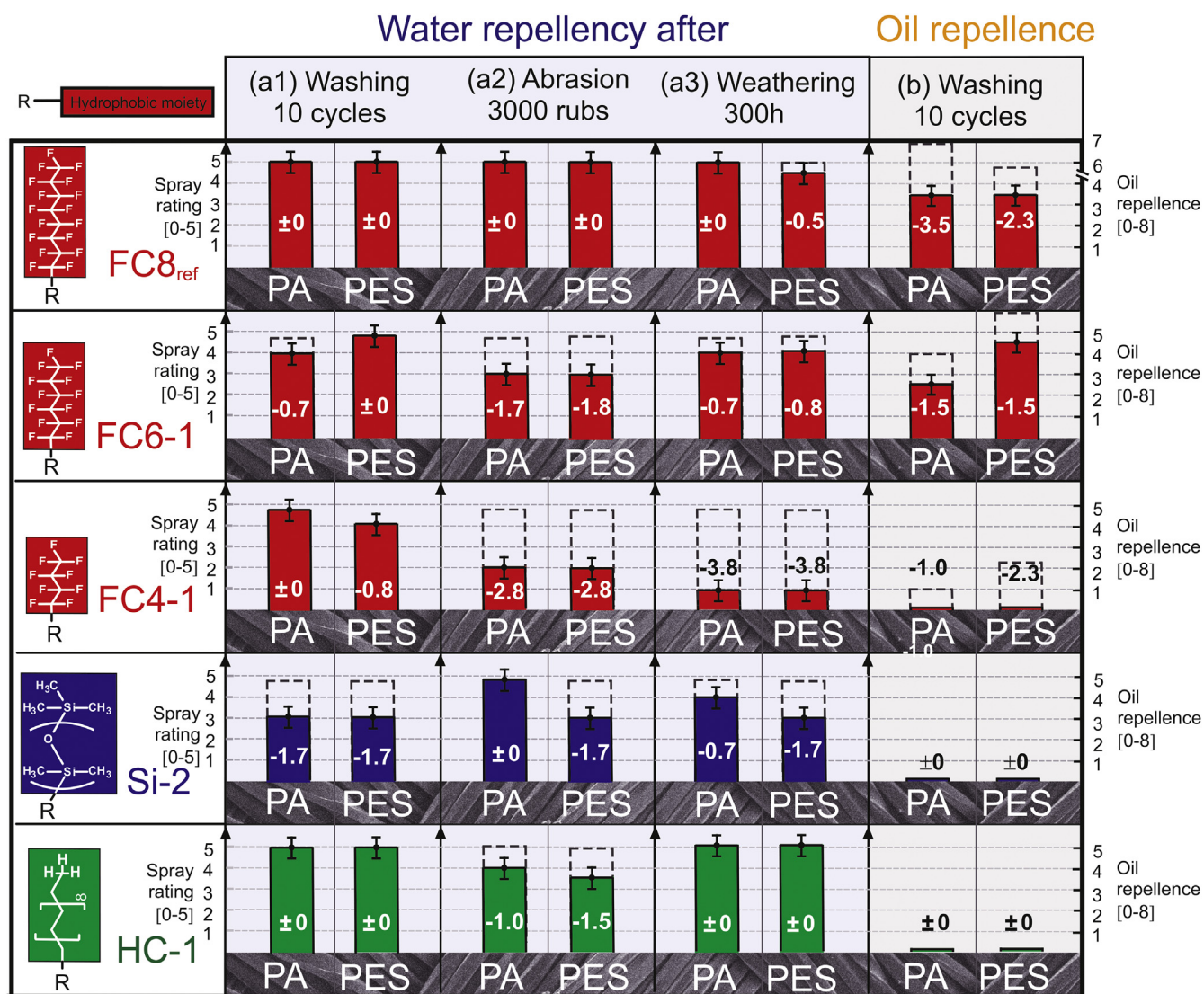


Fig. 4. Selected results of the durability tests for best performing DWR-types on PA and PES-fabrics. Water repellency (a1, spray rating) was tested after 10 washing cycles, abrasion tests and artificial weathering and oil repellency (a2, spray rating) was tested after 10 washing cycles and (b) oil repellency measurements after washing.

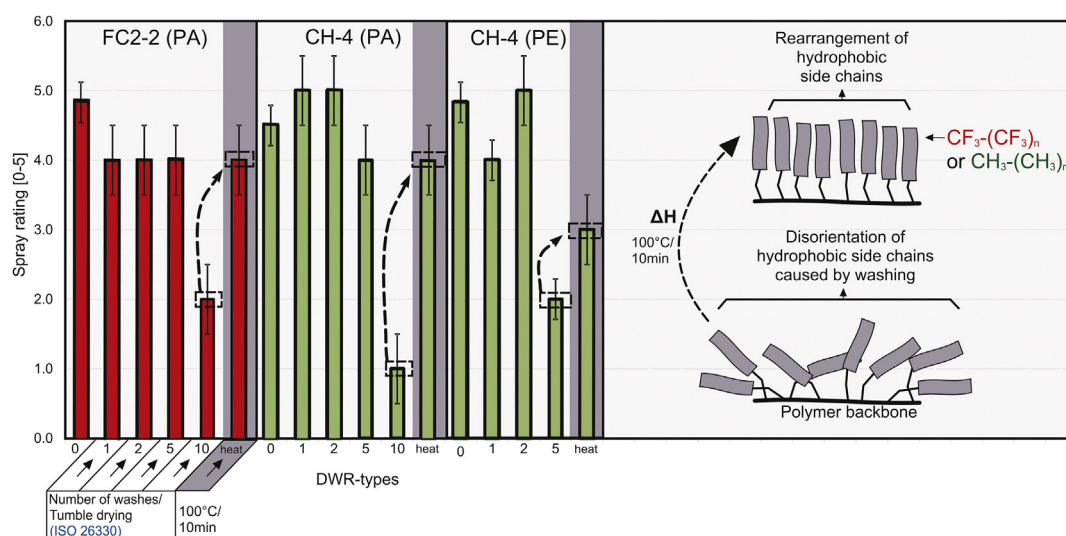


Fig. 5. Reactivation of hydrophobic moieties after heat treatment.

towards the fibre surface and allow a “crystal-like” orientation of either CF_3 - ($\gamma_{\text{sg}} = 6 \text{ mN/m}$ for ideal hexagonal packing (Honda et al., 2005)) or CH_3 - groups ($\gamma_{\text{sg}} = 22 \text{ mN/m}$ Zisman, 1964) at the topmost layer of the DWR-coating (see Fig. 1 a1). Considering that fibres have porous, non-ideal surfaces, the hydrophobic moieties need to be linked to a polymer or particle (organic or inorganic) that allows (1) crosslinking and formation of a continuous and durable film around the fibres and (2) an orientation process of hydrophobic groups with terminal CF_3 or CH_3 groups (Kissa, 2001). This orientation process is crucial for the textile's technical performance since only the first atom layer (Cazabat, 1987) of the fibre's coating is exposed to liquid droplets (e.g. rain) and therefore only the tip of the hydrophobic moieties has a significant influence on the wetting behaviour. When a poor orientation of the DWR molecules occurs, e.g. as consequence of washing without tumble drying, the underlying atoms of less hydrophobic segments (e.g. $-\text{CF}_2-$ with $\gamma_{\text{sg}} = 18 \text{ mN/m}$ or CH_2 with $\gamma_{\text{sg}} = 31 \text{ mN/m}$) become exposed to surface wetting, which results in reduced repellency. An orientation of the DWR molecules to a crystalline structure is governed by flexible carrier polymers (polymer backbone) and also by flexible spacer segments (e.g. $\text{R}_1-\text{O}-\text{CH}_2-\text{CH}_2-\text{R}_2$ or $\text{R}_1-\text{O}(\text{CH}_2)_n\text{N}(\text{R}-)-\text{SO}_2-\text{R}_2$) that link the hydrophobic moieties to the polymer backbone and facilitate conformation processes during elevated temperatures. C8-based long-chain L-SFPs are known for their excellent orientation (Corpart et al., 2001; Bothorel et al., 1992) behaviour, resulting in a crystallization of fluorinated side chains (Honda et al., 2005) (with an optimum for linear (Wang et al., 1997) $\text{C}_n\text{F}_{2n+1}-\text{R}$ chains with $n = 10$ to 12 Kissa, 2001) and thus a consequently denser packing of terminal CF_3 groups (see Fig. 3 a1). This could be confirmed in this study, where C8-based L-SFPs showed the lowest water absorption and highest water repellency (spray_{C8} = 4.8 ± 0.3 ; $m_{\text{H}_2\text{O}-\text{C8}} = 0.08 \text{ g/m}^2$ and $\theta_{\text{C8 L-SFP}} = 148^\circ \pm 6^\circ$) of all DWRs tested on PES and PA outdoor fabrics.

As illustrated in Fig. 3 a1, s-SFPs with shorter chains have a lower packing density since shorter side chains ($\text{C}_n\text{F}_{2n+1}-\text{R}$ with $n \leq 6$) do not crystallize (Honda et al., 2005; Wang et al., 2010). Nevertheless C6 and C4 s-SFPs had high water repellency values, which implies that the degree of side chain orientation seems to have a minor influence on the repellency of water droplets ($\gamma_{\text{H}_2\text{O}} = 72.5 \text{ mN/m}$). Also some non-fluorinated DWRs had high spray ratings and CAs, (eg. spray_{Si-2} = 4.7 ± 0.3 ; $m_{\text{H}_2\text{O}-\text{Si-2}} = 0.36 \text{ g/m}^2$ and $\theta_{\text{Si-2}} = 142^\circ \pm 7^\circ$ or spray_{HC4} = 4.8 ± 0.3 ; $m_{\text{H}_2\text{O}-\text{CH}_4} = 0.11 \text{ g/m}^2$ and $\theta_{\text{HC-4}} = 128^\circ \pm 8^\circ$) which implies an orientation of their hydrophobic moieties. “Wax-like” side chains of n-alkyl acrylate HCs were found to have an optimum for crystallization at chain lengths of 12–18 carbons (Greenberg and Alfrey, 1954), which is similar to the crystallization of wax-tubules in the lotus plant (Dora and Wandelt, 2011).

Another study with alkylsilane ($(\text{C}_2\text{H}_5-\text{O})_3-\text{Si}-\text{O}-(\text{CH}_2)_n-\text{CH}_3$) on cotton/polyester based on fabrics, which are similar to Si-based DWRs, demonstrated a high water CA ($>130^\circ$) for $n > 12$ (Mahlitig et al., 2005). These examples illustrate how a different molecular architecture can influence the water repellency of DWR-related polymers in textile applications.

A different liquid wetting behaviour was observed in this study when it comes to oil repellency which was tested using an industrial standard method (Grajeck and Petersen, 1962) and describes an extreme case of liquid resistance using different oils with very low surface tensions ($31.5 \text{ mN/m} \geq \gamma_{\text{LG}} \geq 19.8 \text{ mN/m}$, see Table S3 in the SM). While a fabric's resistance towards oil is needed for some kinds of protective clothing (Mansdorf and Sager, 1988) used on e.g. oil rigs or for work with non-polar liquids in chemical production facilities, it might be less apparent why consumer textiles need this property. The results showed no oil repellency for all non-fluorinated DWRs (see Fig. 3 a2). While some non-fluorinated

DWR manufacturers argue that garments containing their products are primarily purchased for their water repellency, others argue that protection against staining is a useful fabric property (Slade, 1997). Indeed SFPs are efficient materials for stain repellent textile applications (Rao and Baker, 1994; Türk et al., 2015). Staining of textiles with non-polar liquids can occur when garments encounter oil and grease stains from common machinery (e.g. a bike chain), oil based stains from food (e.g. olive oil with $\gamma_{\text{LG}} \sim 32 \text{ mN/m}$ Deng et al., 2012, chocolate with $\gamma_{\text{LG}} 31\text{--}39 \text{ mN/m}$ Keijbets et al., 2009) or personal care products (e.g. skin lotion).

Staining can also occur “indirectly”, for example, when body sebum, a mixture of “oil-like” hydrophobic triglycerides and wax esters (Smith and Thiboutot, 2008) is deposited on the outside layer of the fabrics. The presence of body sebum is discussed to have an impact on the staining of synthetic fabrics (Bowers and Chantrey, 1969) and also negatively influencing the water repellency. Staining of textiles, however, may reduce the product's lifetime due to an increased amount of laundering or because garments need to be disposed of in cases of irreversible staining. This study confirmed a strong correlation between decreasing perfluoroalkyl chain length of SFPs and decreasing oil repellency (see Figs. 3 and 4). Considering the less optimal orientation behaviour of s-SFPs with lower $\text{C}_n\text{F}_{2n+1}$ -chain length (which do not crystallize), it is therefore more likely that oil droplets are exposed to underlying CF_2 -groups (higher $\gamma_{\text{sg}} \sim 19 \text{ mN/m}$) or even get in contact with much more polar groups e.g. ester groups that connect the side chains to the polymer backbone. This would consequently result in reduced oil repellency, as shown in this study. Washing seems to have a strong effect on the described disorientation process of side chains of s-SFPs resulting in a low oil repellency after washing for the C4 s-SFP. Although side chains of Sis and HCs can crystallise under optimal conditions, the critical surface (γ_c) tension of CH_3 terminal groups is too high to form an oil repellent surface structure. This observation is especially important when it comes to the development of technical protective clothing where the non-fluorinated alternatives might not be an options to deliver sufficient life-saving protection (Siegel et al., 2007; Fung, 2002).

Heating some fabrics that showed a strong reduction in water repellency after washing (5–10 times) to relatively high temperatures ($100^\circ\text{C}/10\text{min}$) after washing showed another aspect of the reorientation process of hydrophobic moieties (see Fig. 5). The analysis was conducted since it was unclear if the loss in water repellency was caused by a gradual wearing of the DWR coating or if it was influenced by disorientation of the hydrophobic moieties. The results after the heat treatment showed that the repellency increased in all the tested cases. High temperatures usually helps the surface segregation (enrichment of hydrophobic moieties) of perfluoroalkyl (Brigden et al., 2013), polydimethylsiloxane (Chen et al., 2000) and alkyl (Greenberg and Alfrey, 1954) groups and can therefore influence the technical performance of DWR-coatings. The experiment provides evidence that the washing process influences the disorientation of the fluorinated side chains. The graph in Fig. 5 illustrates that the drop in water repellency was not caused by the loss of the DWR coating, but suggests that the disorientation of hydrophobic side chains (perfluoroalkyl and alkyl) during the washing process is responsible for the reduced water repellency. Although tumble drying was applied (at 60°C for 30 min) after washing, this thermal energy was not enough to show these effects.

5. Conclusions

The fluorinated and non-fluorinated DWRs were investigated for their technical performance on PA and PES fabrics. DWR products were grouped under consideration of their chemical moiety

providing the water (and oil) repellent function (Holmquist et al., 2016) into s-SFPs and L-SFPs, Sis and HCs. The C8 L-SFP reference material was shown here to have the best properties in terms of initial water and oil repellency as well as durability. The s-SFPs also had comparable initial water repellency and performed well independent of the choice of product and substrate (PA or PES). With regard to durability and oil repellency, technical performance decreased with decreasing perfluoroalkyl chain length. Non-fluorinated DWRs (Sis and HCs) showed more inconsistent results for water repellency and durability. Some novel HC DWRs provided good water repellency and durability when applied to both PA and PES. The fact that some non-fluorinated DWRs failed in an identical experimental setup shows, that these alternative DWRs might need to undergo more extensive selection and optimization processes to achieve product performance comparable to SFPs. None of the non-fluorinated alternatives were able to provide oil repellency, which might limit their use in workwear and also increases the staining tendency of other textiles treated with these non-fluorinated DWRs. Despite their lack of oil repellency, non-fluorinated DWRs have the potential to be used in textile products that only require good water repellency throughout their product lifetime (e.g. waterproof jackets), but there is likely to be a continued niche for SFPs in textile products that require high oil/stain repellency and durability. Nevertheless, especially for the consumer segment of functional textiles, it is important to consider if the benefit of improved material properties of SFPs outweighs the risk associated with the release of highly persistent chemicals into the environment.

Acknowledgements

This research was funded by the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS) under grant agreement no. 2012-2148 (Project SUPFES). The aim of the SUPFES project (www.supfes.eu) is to help industry find alternatives that can replace the prioritised long-chain fluorinated chemicals which are harmful to the environment. We thank our colleagues and project partners at Swerea IVF (present and previous) who are not listed as co-authors but have provided valuable input during the work with this manuscript. We also thank the representatives from the major raw material producers who kindly provided us with valuable information in interview sessions.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2017.11.027>.

References

- Ahlbrecht, A. H.; Brown, H. A.; Samuel, S. 3M patents; Fluorocarbon acrylate and methacrylate esters and polymers. 1957.
- Berger, U., Herzke, D., 2006. Per- and polyfluorinated alkyl substances (PFAS) extracted from textile samples. *Organohalogen Compd.* 68, 2023–2026.
- Bernett, M.K., Zisman, W.A., 1959. Relation of wettability by aqueous solutions to the surface constitution of low-energy solids. *J. Phys. Chem.* 63 (8), 1241–1246.
- Blossey, R., 2003. Self-cleaning surfaces [mdash] virtual realities. *Nat. Mat.* 2 (5), 301–306.
- Bothorel, B., Heller, A., Grosshans, E., Candas, V., 1992. Thermal and sweating responses in normal and atopic subjects under internal and moderate external heat stress. *Archives Dermatological Res.* 284 (3), 135–140.
- Bowers, C.A., Chantrey, G., 1969. Factors controlling the soiling of white polyester cotton fabrics: Part I: laboratory studies. *Text. Res. J.* 39 (1), 1–11.
- Brigden, K., Hetherington, S., Wang, M., Santillo, D., Johnston, P., Greenpeace, 2013. Hazardous Chemicals in Branded Textile Products on Sale in 25 Countries/regions during 2013. Technical Report 06/2013. Greenpeace Research Laboratories, Exeter, UK, p. 47. December 2013.
- Burman, G.W., 2014. Expectations of Durable Water Repellent Fabric Finishes. Cassie, A.B.D., Baxter, S., 1944. Wettability of porous surfaces. *Trans. Faraday Soc.* 40 (0), 546–551.
- Cazabat, A.-M., 1987. How does a droplet spread? *Contemp. Phys.* 28 (4), 347–364.
- Chen, Z., Ward, R., Tian, Y., Baldelli, S., Opdahl, A., Shen, Y.-R., Somorjai, G.A., 2000. Detection of hydrophobic end groups on polymer surfaces by sum-frequency generation vibrational spectroscopy. *J. Am. Chem. Soc.* 122 (43), 10615–10620.
- Corpart, J.-M., Girault, S., Juhué, D., 2001. Structure and surface properties of liquid crystalline fluoroalkyl polyacrylates: role of the spacer. *Langmuir* 17 (23), 7237–7244.
- Davies, A.W., 2014. An Evaluation of the Test Methods Used for Assessing Durable Water Repellent Fabrics within the Outdoor Industry.
- Deng, X., Mammen, L., Butt, H.-J., Vollmer, D., 2012. Candle soot as a template for a transparent robust superamphiphobic coating. *Science* 335 (6064), 67–70.
- Dora, S.K., Wandelt, K., 2011. Recrystallization of tubules from natural lotus (*Nelumbo nucifera*) wax on a Au(111) surface. *Beilstein J. Nanotechnol.* 2, 261–267.
- Ellis, D.A., Martin, J.W., De Silva, A.O., Mabury, S.A., Hurley, M.D., Sulbaek Andersen, M.P., Wallington, T.J., 2004. Degradation of fluorotelomer Alcohols: a likely atmospheric source of perfluorinated carboxylic acids. *Environ. Sci. Technol.* 38 (12), 3316–3321.
- EPA, U., 2006. 2010/2015 PFOA Stewardship Program. United States Environmental Protection Agency, Washington, DC.
- Fung, W., 2002. Coated and Laminated Textiles, vol. 23. Woodhead Publishing.
- Grajcek, E., Petersen, W., 1962. Oil and water repellent fluorochemical finishes for cotton. *Text. Res. J.* 32 (4), 320–331.
- Greenberg, S.A., Alfrey, T., 1954. Side chain crystallization of n-alkyl polymethacrylates and Polyacrylates. *J. Am. Chem. Soc.* 76 (24), 6280–6285.
- Holmquist, H., 2016. Environmental Assessment of Alternative Durable Water Repellent Chemicals.
- Holmquist, H., Schellenberger, S., van der Veen, I., Peters, G.M., Leonards, P.E.G., Cousins, I.T., 2016. Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing. *Environ. Int.* 91, 251–264.
- Honda, K., Morita, M., Otsuka, H., Takahara, A., 2005. Molecular aggregation structure and surface properties of poly(fluoroalkyl acrylate) thin films. *Macromolecules* 38 (13), 5699–5705.
- Hu, J., 2016. Active Coatings for Smart Textiles. Woodhead Publishing, pp. 81–107.
- (ISO), I. O. f. S., ISO 4920, 2012. Determination of Resistance to Surface Wetting (Spray Test).
- (ISO), I. O. f. S., ISO 26330, 2001. Domestic Washing and Drying Procedures for Textile Testing.
- (ISO), I. O. f. S., ISO 14419, 2010. Textiles Oil Repellency-Hydrocarbon Resistance Test.
- (ISO), I. O. f. S., ISO 12947-2, 2016. Determination of the Abrasion Resistance of Fabrics by the Martindale Method.
- Jönsson, C., 2014. A New Research Project on Alternatives to PFASs/PFCs in Textiles... including a Survey to 50 Producers of Outdoor Textiles SUPFES, p. 24.
- Keijbets, E.L., Chen, J., Dickinson, E., Vieira, J., 2009. Surface energy investigation of chocolate adhesion to solid mould materials. *J. Food Eng.* 92 (2), 217–225.
- Kissa, E., 1996. Wetting and wicking. *Text. Res. J.* 66 (10), 660–668.
- Kissa, E., 2001. Fluorinated Surfactants and Repellents. CRC Press.
- Kleiman, J., Tennyson, R.C., 2012. Protection of space materials from the space environment. In: Proceedings of ICPMSE-4, Fourth International Space Conference, vol. 4. Springer Science & Business Media, Held in Toronto, Canada. April 23–24, 1998.
- Knepper, T.P., Frömel, T., Gremmel, C., Driezum, I. v., Weil, H., Vestergren, R., Cousins, I., UMWELTBUNDESAMT (UBA), 2014. Understanding the exposure pathways of per- and polyfluoroalkyl substances (PFASs) via use of PFASs-Containing products – risk estimation for man and environment, p. 133 (UBA-FB) 001935/E 47/2014; UMWELTBUNDESAMT (UBA): Dessau-Roßlau, July 2014. <http://www.umweltbundesamt.de/publikationen/understanding-the-exposure-pathways-of-per>.
- Krafft, M.P., Riess, J.G., 2015. Selected physicochemical aspects of poly- and perfluoroalkylated substances relevant to performance, environment and sustainability—part one. *Chemosphere* 129, 4–19.
- Lavoie, E.T., Heine, L.G., Holder, H., Rossi, M.S., Lee, R.E., Connor, E.A., Vrabel, M.A., DiFiore, D.M., Davies, C.L., 2010. Chemical alternatives assessment: enabling substitution to safer chemicals. *Environ. Sci. Technol.* 44 (24), 9244–9249.
- Li, L., Liu, J., Hu, J., Wania, F., 2017. Degradation of fluorotelomer-based polymers contributes to the global occurrence of fluorotelomer alcohol and perfluoroalkyl carboxylates: a combined dynamic substance flow and environmental fate modeling analysis. *Environ. Sci. Technol.* 51 (8), 4461–4470.
- Mahlitig, B., Haufe, H., Böttcher, H., 2005. Functionalisation of textiles by inorganic sol-gel coatings. *J. Mater. Chem.* 15 (41), 4385–4398.
- Mansdorf, S.Z., Sager, R., 1988. Performance of Protective Clothing: Second Symposium, vol. 989. ASTM International.
- McCann, J., 2005. Material Requirements for the Design of Performance Sportswear, pp. 44–70.
- Mukhopadhyay, A., Midha, V.K., 2008. A review on designing the waterproof breathable fabrics part I: fundamental principles and designing aspects of breathable fabrics. *J. Industrial Text.* 37 (3), 225–262.
- Owens, D.K., Wendt, R., 1969. Estimation of the surface free energy of polymers. *J. Appl. Polym. Sci.* 13 (8), 1741–1747.
- Pan, N., Sun, G., 2011. Functional Textiles for Improved Performance, Protection and Health. Elsevier.
- Rao, N.S., Baker, B.E., 1994. Textile Finishes and Fluorosurfactants. Plenum, New

- York.
- Renner, R., Christen, K., Pelley, J., Thacker, P.D., 2005. Canada bans fluoropolymer stain repellents| Funding woes eroding steam gage network| Cleaning up school bus emissions| Healthy student housing| Mercury in environmental journalists| Honda named greenest brand in 2004| Green facts and figures| Mine tailings soak up greenhouse gas| Pollutants persist in drinking water. *Environ. Sci. Technol.* 39 (3), 56A–60A.
- Ruckman, J., 2005. The application of a layered system to the marketing of outdoor clothing. *Journal of Fash. Market. Manag. Int. J.* 9 (1), 122–129.
- Schindler, W.D., Hauser, P.J., 2004. *Chemical Finishing of Textiles*. Elsevier.
- Shafirin, E.G., Zisman, W.A., 1959. Constitutive Relations in the Wetting of Low-energy Surfaces and the Theory of the Retraction Method of Preparing Monolayers. Naval Research Lab., Washington, DC.
- Shahid-ul, Islam, Mohammad, F., 2014. Emerging Green Technologies and Environment Friendly Products for Sustainable Textiles. In: Muthu, S.S. (Ed.), *Roadmap to Sustainable Textiles and Clothing: Environmental and Social Aspects of Textiles and Clothing Supply Chain*. Springer Singapore, Singapore, pp. 63–82.
- Shahid ul et al., 2013. Green chemistry approaches to develop antimicrobial textiles based on sustainable biopolymers—a review. *Ind. Eng. Chem. Res.* 52 (15), 5245–5260.
- Sherburne, A., Blackburn, R., 2009. Achieving sustainable textiles: a designer's perspective. In: *Sustainable Textiles: Life Cycle and Environmental Impact*, pp. 3–32.
- Siegel, J.D., Rhinehart, E., Jackson, M., Chiarello, L., 2007. 2007 guideline for isolation precautions: preventing transmission of infectious agents in health care settings. *Am. J. Infect. Control* 35 (10), S65–S164.
- Slade, P.E., 1997. *Handbook of Fiber Finish Technology*. CRC Press.
- Smith, K., Thiboutot, D., 2008. Thematic review series: skin lipids. Sebaceous gland lipids: friend or foe? *J. Lipid Res.* 49 (2), 271–281.
- Song, G., 2011. *Improving Comfort in Clothing*. Elsevier.
- Tang, W., Huang, Y., Meng, W., Qing, F.-L., 2010. Synthesis of fluorinated hyperbranched polymers capable as highly hydrophobic and oleophobic coating materials. *Eur. Polym. J.* 46 (3), 506–518.
- Tanner, J.C., 1979. Breathability, comfort and Gore-Tex laminates. *J. Ind. Text.* 8 (4), 312–322.
- Tickner, J.A., Schifano, J.N., Blake, A., Rudisill, C., Mulvihill, M.J., 2015. Advancing safer alternatives through functional substitution. *Environ. Sci. Technol.* 49 (2), 742–749.
- Türk, M., Ehrmann, A., Mahltig, B., 2015. Water-, oil-, and soil-repellent treatment of textiles, artificial leather, and leather. *J. Text. Inst.* 106 (6), 611–620.
- van der Veen, I., Weiss, J.M., Hanning, A.-C., de Boer, J., Leonards, P.E.G., 2016. Development and validation of a method for the quantification of extractable perfluoroalkyl acids (PFAAs) and perfluorooctane sulfonamide (FOSA) in textiles. *Talanta* 147, 8–15.
- Wang, S., Jiang, L., 2007. Definition of superhydrophobic states. *Adv. Mater.* 19 (21), 3423–3424.
- Wang, J., Mao, G., Ober, C.K., Kramer, E.J., 1997. Liquid crystalline, semifluorinated side group block copolymers with stable low energy Surfaces: synthesis, liquid crystalline structure, and critical surface tension. *Macromolecules* 30 (7), 1906–1914.
- Wang, Q., Zhang, Q., Zhan, X., Chen, F., 2010. Structure and surface properties of polyacrylates with short fluorocarbon side chain: role of the main chain and spacer group. *Journal of Polymer Science Part A. Polym. Chem.* 48 (12), 2584–2593.
- Weder, M., 1997. Performance of breathable rainwear materials with respect to protection, physiology, durability, and ecology. *J. Ind. Text.* 27 (2), 146–168.
- Wenzel, R.N., 1949. Surface roughness and contact angle. *J. Phys. Colloid Chem.* 53 (9), 1466–1467.
- Zhang, J., France, P., Radomyselskiy, A., Datta, S., Zhao, J., van Ooij, W., 2003. Hydrophobic cotton fabric coated by a thin nanoparticulate plasma film. *J. Appl. Polym. Sci.* 88 (6), 1473–1481.
- Zimmermann, J., Seeger, S., Artus, G., Jung, S., 2013. Superhydrophobic Coating.
- Zisman, W.A., 1964. Relation of the Equilibrium Contact Angle to Liquid and Solid Constitution. In: *Contact Angle, Wettability, and Adhesion*, vol. 43. American Chemical Society, pp. 1–51.