Abstract

Environmental pollution caused by persistent perfluoroalkyl acids (PFAAs) – organic chemicals with confirmed levels of toxicity and propensity for bioaccumulation – has given rise to global environmental concerns. Functional textiles containing durable water repellents (DWRs) that are based on side-chain fluorinated polymers are noted to be major contributors to the release of such environmental pollutants. This results from the release of impurities and their gradual degradation. Nevertheless, the properties of DWRs based on long chain perfluoroalkyl chains result in exceptional material performance in repellent textiles and are therefore hard to replace without detriment to textile quality. This thesis aims to characterise the currently available DWR alternatives by assessing their technical performance and potentiality as hazardous chemicals with respect to estimated emission scenarios. Furthermore, the work carried out herein suggests that by taking a segmented perspective of the textile market, substitution of fluorinated materials with more environmentally benign alternatives where peak material performance is not required might offer a better solution. In addition, the thesis proposes directions for future research that may be considered essential for a more thorough and robust understanding of the environmental fate of DWR-polymers and how best to reduce diffuse emissions of PFAAs.
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Paper I


My contributions:

(1) Co-authored article (shared first authorship) with Hanna Holmquist (Stockholm University). Developed the idea of the study together with the co-authors.

(2) Performed the research and wrote the corresponding text for the structure-property relationships of durable water repellents (DWRs)

(3) Produced Figure 1

(4) Produced Figures 2 and 3 together with Hanna Holmquist

Paper II


My contributions:

(1) I wrote the article, with contributions from co-authors, and developed the idea of the study together with Philip Gillard.

(2) Performed the sampling application and initial repellency test of alternative DWRs and interpreted the data.

(2) Measured contact angles with the help of special fabric holder construction together with Oscar Levenstam.

(3) Interpreted the data from the durability test of alternative DWRs that were conducted by Anne Star under the supervision of Anne-Charlotte Hanning.

(4) Produced Figures 1-7.
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Stockholm, October
1. Introduction

Ever since humans lost their hair during evolution\(^1\) functional textiles have been the most popular materials for protection against bad weather conditions. Besides insulation\(^2\), a fabric’s repellency\(^3\) is its most fundamental function to ensure the thermal stability of the human body. The invention of rubberized fabrics\(^4\) by Charles MacIntosh in 1823 led to textiles with good water resistance, but poor regulation of human body moisture. They were therefore unsuitable for active outdoor pursuits that increased the body’s liquid loss\(^5\). Since then, various improvements have been made\(^6\),\(^7\),\(^8\) in order to produce durable water repellents (DWRs) that enable fabrics to withstand penetration by water\(^9\) and which also promote the release of body moisture. One of the more successful approaches has been to employ polymers that contain wax- or fatty acid-based hydrophobic groups which form a continuous film around the single fibers of the textiles. This concept combines two mutually contradictory functions, the moisture permeability\(^10\) that is realized by the porosity of the woven fabric and water repellency that is achieved by hydrophobic groups.

The first fluorinated DWRs following this approach were discovered by a technician of the company, 3M, who accidentally spilled some drops of fluorochemical liquid on her shoes\(^11\). When applying different liquids for cleaning purposes, the surface of the shoes appeared to have great liquid repellency towards water, alcohol or other solvents. This observation caused the development of DWRs using side-chain fluorinated polymers (SFPs) in the late 1950s with side chains synthesized through electrofluorination\(^12\),\(^11\) or telomerisation.

Due to their surprisingly properties in creating omniphobic\(^16\) fabrics (repellency towards polar and non-polar liquids), SFPs are up until the present day the predominant polymers used in functional textiles with high product requirements\(^17\). Especially in combination with waterproof membranes (based on stretched polytetrafluorethylene (PTFE)\(^18\)), fabrics with
a multilayered construction revolutionized the outdoor and performance sportswear with materials that were originally developed for space missions or medical applications\textsuperscript{17}. Figure 1 depicts a typical structural building principle and chain length distribution of SFPs based on long perfluoralkyl chains (described as I-SFPs in this work). Despite their great material properties I-SFPs have been found to release persistent, bioaccumulative and toxic perfluoroalkyl acids\textsuperscript{19,20} (PFAAs) such as perfluorooctanoic acid (PFOA) and other perfluoroalkyl carboxylic acid (PFCA) homologues into the environment (see Figure 5). The discharge of these persistent environmental pollutants can be a result of impurities that enter products during production\textsuperscript{21} or gradual degradation of SFPs during the life cycle of textiles\textsuperscript{22}. Consequently, fluorinated DWRs are the subject of worldwide debate\textsuperscript{23} and I-SFPs are therefore part of an ongoing phase-out\textsuperscript{24,25}. Due to the pressure on fluorochemical manufacturers by regulatory authorities\textsuperscript{26}, eight major fluorochemical producers (collectively represented by the FluoroCouncil) joined in a global stewardship program.\textsuperscript{24n} In 2006, members of the FluoroCouncil “voluntarily” committed to eliminate the global use of PFOA and related chemicals through the 2010/2015 PFOA Stewardship Program. The aim was to eliminate manufacture, use and product content by 2015. Additional campaigns, like Greenpeace’s DETOX\textsuperscript{28} focused on emissions from products made by well-known textile brand names\textsuperscript{29,30} with the goal of convincing these brands to switch to more environmental benign DWR alternatives that do not release long chain PFAAs. Presently available DWR raw materials are therefore either based on short chain-SFPs (with $C_n F_{2n+1} \cdot R$ and $n \leq 6$ described as s-SFPs in this work) or non-fluorinated chemistry.

This chemical substitution in consumer textiles, however, took place before alternatives were sufficiently characterised for human health and environmental effects\textsuperscript{31} and technical performance profiles. The s-SFPs still utilize the structural principles of the I-SFPs while substituting the long perfluoroalkyl side chains with shorter ones. In addition to the s-SFP-based DWR products, the current market is characterized by a growing number of non-fluorinated DWR-products often marketed through assurances of good technical performance and benign environmental fate.
1.1 The SUPFES project—how Academia and Industry work together

The four-year multidisciplinary venture “Substitution in Practice of Prioritized Fluorinated Chemicals to Eliminate Diffuse Sources” (SUPFES) aims to characterize and decrease the diffuse emissions of PFASs and other priority environmental pollutants in consumer textiles. The different research groups and core competences are illustrated in Figure 2. As can be seen from the figure, the four organizations conducting the research in the project are the academic institutions of Vrije University (VU) Amsterdam in the Netherlands, Stockholm University (SU) and Chalmers University, and the textile research institute Swerea IVF. Multiple stakeholders are also closely involved in the SUPFES project, namely; governmental authorities (e.g. the Swedish Chemicals Agency (KEMI)), the fluorrochemical manufactures (e.g. 3M and Chemours), textile producers (e.g. Haglöfs) and nongovernmental organizations (NGOs, e.g. the Swedish Society for Nature Conservation). The collaboration with industrial stakeholders has made it possible to generate experiments on DWR-polymers that are similar to those used in the textile industry.

Figure 2: Schematic representation of the international consortium that carry out the research in the SUPFES project and their different core competences. Researchers in academia work together with the textile research institute, Swerea IVF. The figure also illustrates the importance of stakeholder involvement.

The aims of the project are to: i) characterize the diffuse emissions of critical environmental pollutants (e.g. PFAAs but also cyclic siloxanes like D4 (octamethylcyclotetrasiloxane) and D5 (decamethylcyclopentasiloxane) from consumer products such as textiles, and ii) compare the a) technical performance and b) environmental impacts of alternative
DWRs to those based on l-SFPs. The goal is to help industry find DWR alternatives that can provide technical performance and at the same time be environmentally benign. SUP-FES also intends to provide policy makers with a basis for legislation and industry with guidelines for ensuring reduced human health and environmental impacts\textsuperscript{31}.

1.2 Textile repellency

Textile’s repellency is a property that often stays unnoticed until it starts raining or other liquids gets spilled over a fabric’s surface. Modern fabrics consist of complex fiber assemblies\textsuperscript{32} with open pores and a surface structure defined by the woven yarns and different fabric constructions. Therefore, the interaction of liquids and with textile surfaces is a complex process and different wetting phenomena can be observed on these non-ideal surfaces (see Figure 3 a3-a5).

For an effective substitution of chemicals related to functionality of DWRs, it is beneficial to understand the repellency of textiles at a macro and microscopic scale. Repellency is defined as a condition of limited wettability\textsuperscript{9}. The interaction of liquids and textiles\textsuperscript{33} depends mainly on their fiber geometry, the capillary geometry (pores between the fibrous assemblies), the amount and chemical nature of the liquid and the wettability of the fibers. The latter can be influenced by the DWR coating (see Figure 3a). When it comes to protection under heavy weather conditions, the production of efficient water repellent fabrics is of great practical importance\textsuperscript{34}. Regardless if water droplet are falling in a cloud burst\textsuperscript{35} (with high hydrostatic pressure average droplet diameter \(~0.3\) mm; terminal velocity \(~25\) km/h and \(E_{\text{Kinetic}} \sim 346 \times 10^{-6}\) Nm per droplet) or as drizzle\textsuperscript{35} (with much lower kinetic energy droplet diameter \(~0.02\) mm; terminal velocity \(~3\) km/h and \(E_{\text{Kinetic}} 0.0012 \times 10^{-6}\) Nm per droplet) on textiles, a droplet deposited on an optimal DWR-treatment will form high contact angles (CA) and will roll off easily from the garments. Figure 3 shows an example of a typical layered fabric construction\textsuperscript{10} of high performance rain gear that consist of a water repellent fabric with DWR-treatments (see Figure 3 a), a waterproof membrane (see Figure 3b) and an a inner fabric (see Figure 3c) that holds the different materials together and stabilizes the waterproof membrane. The single fibers in the outer fabric are coated with DWR-polymers (see Paper I and II) and these chemical moieties (see Figure 3a1) form an “umbrella-like” hydrophobic shield which transfers the woven fabric into a surface near to the superhydrophobic state\textsuperscript{36} (surfaces with water contact angles of \(\theta_w > 150^\circ\)).
Figure 3: Schematic representation of a layered waterproof and breathable fabric (simplified) and its moisture regulation through the fabric with: (a) an external fabric that consists of a woven fiber material that is (a1) coated with a crosslinked DWR-polymers containing different hydrophobic moieties and ideally results in textiles that show “Cassie-Baxter” like liquid repellency. This optimal repellency can be reduced by high hydrodynamic pressure and/or an inefficient DWR-treatment that results in a reduced repellency of (a3) the “Wenzel state” or (a4) in the worst case a complete wet-out is caused by the liquid’s penetration into the pores of the weave called “wicking” and (b) a porous membrane based on stretched PTFE or membranes with hydrophilic channels that are stabilized through (c) an inner fabric.

Due to the combination of hydrophobic fibers and a rough surface of fibrous assemblies, water droplets minimize their contact area (and surface free energy) to the textile surface resulting in the “Lotus-like” Cassie-Baxter wetting with air trapped below the drop. This causes consequently a very low adhesion and water droplets are easily repelled without leaving water films between the fibers. If the DWR treatment has reduced efficiency or the hydrostatic pleasure increases (e.g. water waves crashing over a boat during sailing), water wet the fabric surfaces according to the Wenzel state, where water droplets form high CA but are pinned to the fabrics (see Figure 3 a3) and therefore not easily repelled. Outdoor garments with this behavior would still be repellent, since the water would not penetrate into the pores of the weave but the user could sense a difference in the macroscopic repellency. If the DWR treatment is insufficient, water droplets wet the woven fabrics completely, a phenomenon called “wicking” (Figure 3 a4) resulting in a wet-out (the outer fabric absorbs water). Even if wet out occurs, the membrane offers another barrier towards water. The complete wetting of the outer fabric, however, can cause a significant cooling of the wearer and a “wet feeling” due to a thermal bridges caused by water.

The best results for DWR-treatments have been achieved with comb-like polymers based on I-SFPs (with side changes based on $C_nF_{2n+1}$–R with $n=8$ see Figure 1) and the
switch to short chains s-SFPs showed a reduced textile repellency, at least in early products\textsuperscript{41}.

Even more challenging is to create textile repellency against liquids that differ from water in their polarity and surface tension such as biological fluids or oily stains\textsuperscript{35}. Liquids with lower polarity and consequently lower surface tension are not so easily repelled by textile fabrics. This is particularly important when it comes to technical protective clothing where DWRs deliver a lifesaving functionality (see Figure 7).

1.3 Aims and objectives of the thesis.

1) Identification of the main data gaps for currently used DWRs for textile applications with regards to their, structure property relationships, technical performance and environmental fate (Paper I).

2) Provide a comprehensive technical performance screening of relevant alternative DWRs in comparison to l-SFPs (Paper II).

3) Describe the future research directions within this doctoral project.
2. Summary of papers

2.1 Paper I: Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing

Background

This critical review combines the identification and description of alternative DWR chemistry and the characterization of the hazards associated with chemicals likely to be diffusely released from these DWR-treatments. Emissions are expected to occur via two possible pathways; (I) the leaching of impurities from chemical production that are not bound to the fabric fiber and (II) gradual degradation of DWR-treated products during the use-phase and degradation of fiber fragments or particles lost from woven fabrics by mechanical stress. The paper also identified major data gaps when it comes to the environmental behavior of DWR-polymers.

Methods

![Figure 4: Schematic representation of the approach to (a) identify alternative DWR chemistry, (b) estimate the emissions of chemicals and (c) the hazard assessment related to these chemicals.]

Since DWRs are of high commercial interest, the molecular structure is often a trade secret and only a limited amount of open access literature describes the presently used DWR-chemistry in detail. Therefore, other non-conventional sources (e.g. the patent literature, interviews with industry) were used for obtaining relevant information.
Results

The review of different accessible sources (see Figure 4) showed that DWR alternatives can be divided into four broad groups that reflect their basic chemistry: side-chain fluorinated polymers, silicones and hydrocarbons that represent the hydrophobic moieties. These moieties are bonded to a polymer backbone that allows the formation of a DWR-film on the individual fibres of the fabrics. The fourth group referred to as “other chemistries” in the paper is based on the same hydrophobic moieties that are bound to organic or inorganic particles (includes dendrimer and inorganic nanoparticle chemistries). Structures of modern DWR-polymers are often copolymerized with hydrophilic segments that deliver certain fibre affinity or solubility of the emulsions. The results showed that there are large differences in performance between the alternative DWRs, most importantly the lack of oil repellency of non-fluorinated alternatives.

The results also showed that for all alternatives, impurities and/or degradation products of the DWR chemistries are diffusively emitted to the environment. The pathways of critical chemicals into the environment are complex and can occur (I) during the textile finishing process in the textile mills (II) during the use phase, due to wear and tear (III) after disposal (e.g. in landfills) or incomplete combustion processes. An example of loss processes that can occur during the use-phase of textiles which have been treated with I-SFPs is the release of PFOA (and higher homologues), which is portrayed in Figure 5. Textiles with alternative DWRs will undergo comparable loss processes resulting in the release of a wide variety of different substances, depending on the initial chemistry. Nevertheless, the loss during finishing and after disposal of textiles will differ widely and to foresee it requires a deeper understanding of these processes.

Our hazard ranking suggests that hydrocarbon-based DWRs are the most environmentally benign, followed by silicones and the side-chain fluorinated polymer-based DWR chemistries. Industrial commitments to reduce the levels of impurities in silicone based and side-chain fluorinated polymer based DWR formulations will lower the actual risks. Furthermore, the following major data gaps were identified and will be addressed throughout the future work within the SUPFES project.

1. Some alternative DWRs showed improved hazardous properties compared to legacy I-SFP DWRs, but up until now it is unclear to what extent environmentally benign alternatives can be used to meet the different user needs and fulfil certain technical performance criteria.

2. A number of data gaps were identified in the hazard assessment, especially for the degradation products of the silicone DWRs. The group of “other chemistries”, including dendrimers and inorganic nanoparticles, was not possible to characterize at all due to the lack of information on these structures.

3. The relevance of the loss scenarios needs to quantified with environmentally realistic experiments.
Figure 5: Possible mechanisms (simplified) for loss of (g) PFOA from DWR treated fabrics during (II) the use phase for the example of DWRs based on long-chain C8 PFASs with (a) cleavage of the polymer backbone by UV-light into oligomeric/polymers, (b1) the evaporation of the 8:2 FTOH as residual from the fabric, (b2) the transformation of 8:2 FTOH in the atmosphere into PFOA, (b3) the rain-out of water soluble PFOA from the atmosphere, (c) the wash-out of water soluble residuals like PFOA or water soluble monomers, (d1) the loss of particles and fibre fragments caused by abrasion containing the C8 side-chain fluorinated polymer based DWR treatment which might undergo further degradation processes (d2) in the environment, (e) the hydrolysis of C8-side chain during laundering and the loss of DWR-coated fibre fragments during the washing process into the effluent, (f) the release of DWR-coated fibre fragments via the wastewater treatment plant and the further transformations of these precursors in PFOA.
2.2 **Paper II: Performance evaluation of state-of-the-art durable water repellents for PA and PES fabrics.**

**Background**

Paper 2 provides an overview of the technical performance of currently available fluorinated and non-fluorinated alternative DWR technologies for textiles which were identified in paper 1.

**Method**

![Diagram](image)

**Figure 6:** Schematic representation of the SUPFES approach for the DWR-selection process and experimental setup with (a) the identification of state-of-the-art DWR-chemistry (b) grouping of the formulations into side-chain fluorinated polymers (SFPs), silicones (Sis) and hydrocarbons (HCs) and (c) the DWR selection that involved consultation with major raw material suppliers including nondisclosure agreements (NDAs)

DWRs were grouped in this study according to their ability to provide water (and oil) repellency (see Figure 6b) and according to their expected environmental fate. DWRs were applied and tested for repellency using industrial standard and complementary methods. Since the repellency and durability over the garment’s lifetime strongly depends on the choice of DWR-formulation, curing conditions, industrial expertise and empirical trials, 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 way that was similar to those used in the textile industry under industrial conditions.
Results

Most short-chain SFPs and non-fluorinated DWRs showed excellent water repellence and durability while short-chain SFPs were the more robust technology. A strong decline in oil repellency with perfluoroalkyl chain length was determined for fluorinated DWRs. Non-fluorinated alternatives did not repel oil at all.
3. Discussion

Through the collaboration within the SUPFES project and the critical review paper (paper I) about alternative DWRs for textile applications, major data gaps could be identified that limit the complete evaluation necessary to substitute I-SFPs with environmentally benign alternatives. Indeed, it is questionable if a certain DWR-technology should be favored over another one based on current knowledge as such a decision requires a comprehensive understanding of properties and environmental behavior of DWR-polymers. This applies for their technical performance (paper II) as well as for their environmental behaviour (paper I). Although most alternatives DWRs have a favourable hazard profile compared to legacy I-SFPs (see paper I), they all release impurities and/or degradation products into the environment and the precise characterization of the complex loss processes (see paper I section 4) has not been conducted. Although “prominent” examples of long-chain perfluoroalkyl acids like PFOA are found and extracted in textiles in several studies, loss scenarios for technical DWR-polymers (see Figure 1) are likely to result in complex precursors including particles, fibre fragments or oligomeric breakdown products. This release of large molecules and particles could result from material stress during the use-phase of textiles and once released into the environment could slowly degrade to release, for example, more PFAAs. In addition, the production of textiles during the fibre treatment process could be another source of environmental pollutants when run under inadequate process conditions. Last but not least, the disposal of textiles could be important for the fate of DWR-finishes. Both waste incineration and disposal in landfills seem to be not unproblematic for fluorinated materials given their extreme resistance to degradation.

All these aspects should be considered when assessing DWR alternatives for their long and short term environmental impacts. Particular attention should be given to DWR alternatives that release persistent and/or toxic compounds. For example, the s-SFPs, which are currently the material of choice when it comes to high performance applications (see paper II) can release precursors that will degrade into perfluorobutane sulfonic acid (PFBS) and perfluorohexanoic acid (PFHxA). These substances have, similar to their higher homologues (PFOA and PFOS), negligible environmental degradation half lives and environmental concentrations will likely rise and be difficult to reverse. This argument might also be true for impurities released from other DWR alternatives such as cyclic siloxanes that have high degradation half-lives in certain environmental media (e.g. in aquatic sediments).

Furthermore, it is still unclear if textiles with DWR-treatments are a major source of environmental pollutants like PFAAs and no systematic studies have been presented so far.
Nevertheless, consumer outdoors textiles (estimated with 23 billion USD in sales for 2018\textsuperscript{52}) are produced for a mass market and the global production of SFPs was roughly estimated by Knepper et al. at 15,000 tonnes per year\textsuperscript{20} (~10\% of the total fluoropolymer production). Considering these high production estimates, the identified loss scenarios from DWR treated textiles (paper I) and the fact that industrial processes sometimes might not run under optimal conditions\textsuperscript{53} (e.g. bad curing conditions), defuse emissions caused by functional textiles should be a topic of further investigation.

Experiments are necessary to quantify loss processes under realistic conditions and help to estimate total emissions. This quantification needs to be combined with a mechanistic explanation of the loss processes identified in paper I. Determining the breakdown of SFPs with analytical methods is challenging since technical DWR-products consist of complex polymer structures with a distribution of molecular weight. Furthermore, a good quantification of emissions needs a deep understanding of production conditions and consumer behaviour including disposal scenarios. In particular, conditions during the production of consumer textiles at the fibre finishing process are often hard to assess. The constellation of industrial stakeholders which are part of the SUPFES-project (see Figure 2) should help to base our further research on realistic assumptions, if they are willing to provide us with the necessary information.

Another perspective on a successful substitution of I-SFPs with alternative DWRs could consider consumer needs. DWR-finishes (as shown in Figure 7, published as Fig. 3 in paper I) have to fulfil a broad range of performance requirements depending on their end-use. The figure opens up the hypothesis that not all textiles necessarily need the highest liquid repellency. The investigations of paper II showed an excellent in the technical performance of non-fluorinated alternative DWRs in some applications. Since “the overlap between outdoor, active wear, and lifestyle dressing is increasingly muddled”\textsuperscript{54} it might be reasonable to reconsider where S-SFPs deliver essential functionalities and where environmental begin alternatives are suitable substitutes for I-SFPs.
Figure 7: Illustration of the increased need for technical performance (here in essence degree of oil repellency and durability of oil- and water repellency) with more advanced user needs; advancing from fashion to comfort to hazard management. Examples of garments meeting user needs within the fashion segment are e.g. jackets primarily chosen based on looks (design, colour etc.) and never or seldom used in weather conditions requiring water repellency. Garments within the comfort segment could be e.g. jackets often used in weather conditions requiring water repellency to stay warm and dry but where the user can find shelter within a reasonable time and thus is unlikely to experience a life threatening situation due to failing water repellency. Finally, garments in the hazard management segment must be water (and sometimes oil) repellent for protecting the life of the wearer. Garment types (A–H) were subjectively placed in the graph and further work is needed to quantify the metrics on the graph’s axes.
4. Future work

Future research within this doctoral project in cooperation with the other SUPFES members will include a broad environmental assessment (i.e. risk and life cycle assessment (LCA)). This work will be led by the colleagues at Chalmers University (see Figure 2). So far we have only considered impacts from emissions during the use phase. Further investigations within the SUPFES project will focus on the environmental fate and effects of chemicals released from alternative DWRs during their entire life cycle. This will include (I) production during the fiber treatment process, (II) additional releases during the use-phase from wear and tear and (III) releases after disposal which will include incineration, the transfer to landfills and sewage sludge applied to agricultural land.

Project I: “Strategies for replacing persistent polymers in textile finishing based on the consumer perspective”. This study aims to further evaluate the potential of non-fluorinated DWRs by readdressing consumer needs and technical functionality in DWR outdoor apparel. For this purpose, SU will cooperate with researchers of the University of Leeds who collect data to evaluate the consumer needs in relation to different outdoor clothing segments that use DWR-treatments (see Figure 3 D-H). Results of this survey will be combined with data from practical experiments conducted at the textile research institute Swerea IVF (see Figure 2). The results of paper II showed some encouraging water repellency and durability results for alternative non-fluorinated DWRs, but non-fluorinated DWRs did not repel oil. While the oil repellence (ISO 14419) is tested using different non-polar oils with a very low surface tension (see methods in paper II), the majority of stains can be repelled more easily by textile surfaces (see 1.2) since they do not contain a large amount of lipids (e.g. coffee; red wines) which results in their intermediate polarity and higher surface tension values. Some preliminary experiments with non-fluorinated DWR-polymers that were optimized by one of SUPFES’s industrial stakeholders to stain repellency of the PA and PES fabrics (see materials paper II) showed promising first results with liquids of intermediate polarity. Additional first results from the consumer survey indicated that stain repellency might be not a major criterion for purchasing an outdoor garment. This project will critically evaluate where the highest technical performance of fluorinated DWRs in consumer textiles are needed and where environmental benign materials could deliver alternative solutions.
**Project II:** “Determining emissions from textiles containing durable water repellents based on side chain fluorinated polymers”. This study will quantify and characterize total emissions from with DWR-treated fabrics (based on I- and s-SFPs). A high number of fabrics (≥ 10 replicates) with DWR-treatment will be exposed to stressors like washing, weathering (artificial and real weathering test in Australia with exposure to a broad-spectrum UV radiation of up to 1kW/m²) and abrasions, to simulate a garments life length. Emissions will be quantified using Combustion Ion Chromatography (CIC) at SU and by using Particle Induced Gamma-ray Emission (PIGE) in cooperation with the Oregon State University. Both methods will determine the total loss of organofluorine before and after application of combined stress parameters to the fabrics treated with I- and s-SFPs. Preliminary experiments conducted by researchers at VU Amsterdam (see Figure 2) indicate that the DWR-coating applied to the fabrics in a discontinuous padding process (see methods in Paper II) is relatively evenly distributed over the fabric, which is an important condition to determine loss processes. Until now, it is unclear if the available methods are sensitive enough to measure the differences in fluorine losses and make precise emission estimates. Nevertheless, reduction of the macroscopic repellency (seen e.g. in Figure 7 in paper II) is an indication that major changes happen to the textile surfaces during the durability tests.

**Project III:** “A mechanistic study of emissions caused by gradual degradation processes of Textiles with SFPs” This mechanistic study of the “visual” (microscopic) changes of the fibre surface (see Figure 3) after applying mechanical stress like the Martindale abrasion test (see methods paper II) will be conducted with scanning electron microscopy (SEM) at the textile research institute Swerea IVF. A more advanced analysis of the degradation processes of SFP-based DWRs with the help of high resolution mass spectrometry could be an approach for an improved mechanistic understanding of gradual degradation processes. Since mobile, non-volatile breakdown products of SFPs will have a high affinity to the surface of the remaining DWR-coating on the fibres (due to fluorophobic interactions similar to process that occur during side chain crystalisation), it might be possible to extract and analyze more complex precursors of PFAAs. This method could confirm the presence of the predicted degradation products from loss processes identified in paper I. A similar approach was already used by Soeriyadi at all to study the degradation behavior of acrylic model polymers (poly(hexafluoro butyl methacrylate)) exposed to temperature and UV-light on a molecular level. The identification of gradual degradation (e.g. oligomers) products could result in a better understanding of loss processes from consumer textiles and be a complementary method to the targeted analysis of textiles conducted at VU-Amsterdam.
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