Invited lecture/Review

Unveiling PFAS-free Solutions for Hydrophobic and Oleophobic Textile Coatings

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Abstract:
Per- and polyfluoroalkyl substances (PFAS) are a large group of synthetic compounds containing carbon-fluorine (C-F) bonds. They are used in almost all industries, including the textile industry, to impart hydrophobic, oleophobic, stain-repellent or non-stick properties to various materials. They are also valued for their excellent thermal, chemical and mechanical stability. However, increasing environmental and health concerns about PFAS have led to an urgent need to find sustainable alternatives. Due to their chemical composition, which contains strong carbon-fluorine bonds, they are difficult to degrade and tend to bioaccumulate in the environment and in human tissue. Human exposure to PFAS has been linked to a number of adverse health effects, including immunosuppression and cancer. As a result, academia and industry are increasingly focused on developing alternatives to PFAS in a variety of applications, to reduce the environmental and human health impacts associated with these persistent substances. This review article explains the basic properties of PFAS, the principles of textile wettability and discusses possible PFAS-free solutions in the field of environmentally and human friendly hydro-/oleophobic textile coatings.

Keywords: PFAS, hydrophobicity, oleophobicity, bio-based, coatings, textile

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1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a large group of synthetic chemical compounds containing carbon-fluorine bonds. They are highly valued in various industrial applications due to their exceptional thermal, chemical and mechanical stability. As reported by the Environment Directorate of the Organisation for Economic Co-operation and Development (OECD), there are more than 4,700 different chemical compounds that belong to the PFAS family (OECD, 2018). PFAS are mainly known for their hydrophobic and oleophobic properties, which means that they impart water and oil repellent properties to treated surfaces. However, as they contain carbon-fluorine (C-F) bonds, which are among the strongest bonds in organic chemistry, they are difficult to degrade. As a result, their persistence in the environment, bioaccumulation and potential adverse effects on the environment and human health have raised significant concerns. As a result, the science and industry are increasingly focussing on developing alternatives to PFAS in various applications, including textiles, to reduce the environmental impact associated with these persistent substances.

2. PFAS in the textile industry

PFAS have played a pivotal role in the textile industry as coatings to improve repellent properties of textiles. Moreover, textile industry is considered the largest PFAS consumer, accounting for approximatelly half of the worldwide PFAS use (Lassen et al., 2015). Due to the uniquefunctional, mechanical, chemical and thermal properties, they are especially used for products that need to be exceptionally durable under various conditions. Their ability to repel water and oil allows coated surfaces to be highly resistant to stains and liquids, making them essential for safety, health and comfort, in the protective, medical or apparel industry. The most common water and oil-repellent products found in textiles are sportswear, leisure wear, uniforms, workwear, upholstery and automotive fabrics, awnings, sunblinds, curtain fabrics, tents, umbrellas, table and bed linen and carpets (Schindler & Hauser, 2004). They are often found under trade names such as NanoTex and GoreTex (Zheng & Salamova, 2020).

2.1 PFAS properties

Generally, PFAS are divided into two main groups: polymers and non-polymers (**Figure 1**). While the polymer group includes two commonly used materials, polytethrafluoroethylene (PTFE, Teflon) and ethylenetetrafluoroethylene (ETFE, Tefzel), the non-polymers are more often commonly in the environment (Meegoda et al., 2020). Non-polymeric PFAS are categorised into subgroups depending on whether hydrogen atoms are completely (perfluorinated) or largely (polyfluorinated) replaced by fluorine atoms (Brunn et al., 2023).

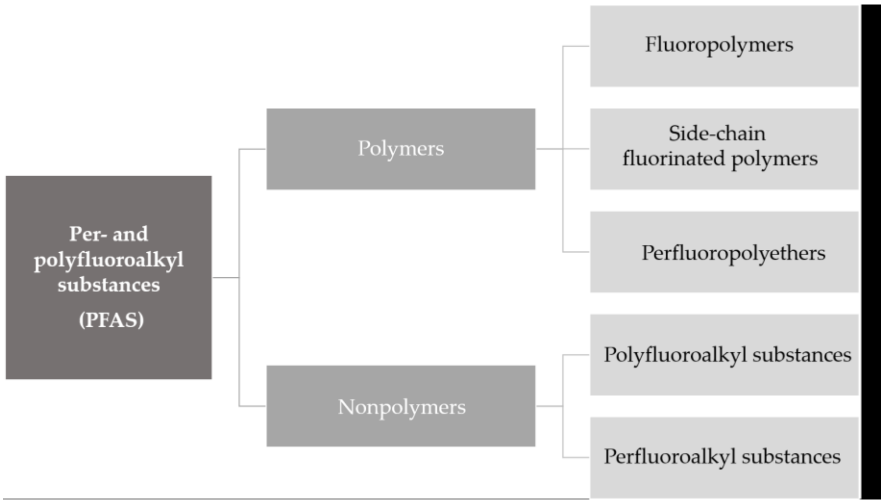

Figure 1. Classification of PFAS compounds, adapted from Meegoda et al., 2020.

This is especially important because the exceptional durable and functional properties of PFAS are closely linked to their chemical composition. The unique properties result from the presence of fluorine atoms bonded to a carbon backbone, which leads to a strong and stable molecular structure. The high electronegativity and small size of fluorine make the C-F bond one of the strongest covalent bonds, which means that a large amount of energy is required to break it (Meegoda et al., 2020). This robust chemical structure gives them remarkable thermal, chemical and mechanical resistance.

To achieve water, oil and stain-repellency of textiles, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are mainly used, which belong to the nonpolymeric perfluroalkyl substances group. Due to the existing restrictions on the use of PFOS and PFOA (Pontius, 2019), PFAS with shorter carbon chains, that are less persistent are also used (Zheng and Salamova, 2020). However, the chemical structure (especially the length of the carbon chain) strongly influences the properties of the compound. Long-chain PFAS compounds are associated with increased hydro-/oleophobicity (Meegoda et al., 2020).

2.2 *Basic principles of textile surface wettability*

Three different types of repellencies can be achieved by modifying the surface of textiles. The first is hydrophobicity, where the water droplets do not spread or wet the surface of the textile fabric. The second one is known as superhydrophobic or ultrahydrophobic, in which the contact angle between the liquid droplet and solid surface (θ) (**Figure 2**) is greater than 150° and the droplet has a small slip-off angle (Shirtcliffe et al., 2010; Ueda & Levkin, 2013), meaning that superhydrophobic fabrics do not only repel water, but also allow the water droplet to roll off the surface. This phenomenon can also be found in nature and is known as the lotus leaf effect, which has a self-cleaning effect due to the high surface roughness. The third type of repellency is oleophobicity, where the surface repels oily liquids.

The boundary between wetting and repellency is defined by the contact angle of the liquid droplet on the textile substrate (**Figure 2**). If the contact angle is less than 90°, the textile is wettable, but if the contact angle is greater than 90°, the textile substrate is repellent. In other words, an increase in the contact angle means an increase in repellency.

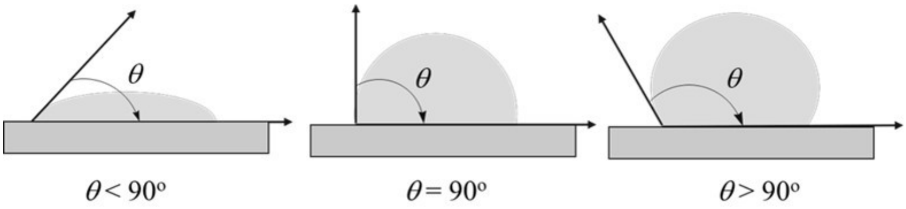

Figure 2. Wetting or repellency depending on the contact angle of the liquid droplet (θ).

We outline two theoretical models that describe the wettability of rough and heterogeneous (non-uniform, consisting of different chemistries) surfaces, the Cassie-Baxter and the Wenzel model (Huang & Gates, 2020; Roach et al., 2008; Crick & Parkin, 2010; Wang et al., 2020). According to Wenzel, the water droplets have full contact with a rough surface, and there are no air pockets under the liquid droplets (Shahid et al., 2022; Crick & Parkin, 2010). According to the Cassie-Baxter model, a water droplet sits on top of a rough surface, due to the trapped air between the grooves of the rough surface. The area where the air is trapped is not wetted by the liquid, creating a separation between the liquid and the grooves of the rough surface (Shahid et al., 2022; Darband et al., 2020).

Achieving good repellency is to a large extent dependent on two properties, surface energy and surface roughness. The surface energy depends on the chemical structure of the surface and can be altered by chemical modification of the fibres (Simončič, 2012). In order to achieve a water and oil repellency it is necessary to reduce the surface energy of the fibres. Roughness, or more specifically nanoroughness, can be achieved by changing the morphology of the fibres through the application of coatings containing nanoparticles or nanocomposite films.

Applying a repellent coating to the surface of the textile changes its properties by reducing the surface free energy of the fibres. The extent to which the surface free energy of the finished textile is reduced depends on whether it is hydrophobic or oleophobic. The lower the surface free energy of the fibre, the less wettable the fabric is. The critical surface energy or surface tension (γ_C) of fibres must be much lower than the surface tension of the liquid (γ_L) that is being repelled (Schindler & Hauser, 2004). Commercially available repellents contain either hydrocarbon or perfluorinated hydrocarbon groups in their chemical structure. If the repellent contains a hydrocarbon chain (**Figure 3a**) in its structure, it lowers the surface energy of the substrate to 22–30 mN/m (Simončič, 2012). Such a surface is only water repellent because the surface free energy is lower than the surface tension of water (73 mN/m) (Schindler & Hauser, 2004), but not lower than the surface tension of oils (30–40 mN/m) (Simončič, 2012). If the repellent has perfluorinated hydrocarbon groups (**Figure 3b**) in its structure, it reduces the surface energy of the substrate to a value 6–30 mN/m, providing oil repellency in addition to water repellency (Simončič, 2012). In this case, the surface free energy is much lower than the surface tension of the oils.

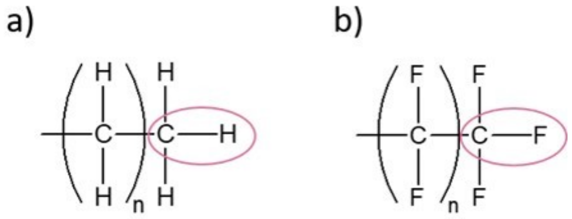

Figure 3. A hydrocarbon chain (a) which is included in the structure of commercial water repellents and perfluorinated hydrocarbon groups (b) which are included in the structure of commercial oil repellents.

Another principle for achieving repellency of a textile material is by increasing surface roughness. This can be achieved by changing the morphology of the fibres. On a rough hydrophobic surface, the contact area between the water droplet and the surface is reduced. The water droplet sits on the grooves of such rough surface and forms an almost spherical shape with a high contact angle (**Figure 4**). The presence of air pockets increases the interfacial area between water and air and decreases the interface between the solid and water. The water droplet sits partly on a solid surface and partly on air pockets, which greatly reduces the adhesive forces between the water and the solid.

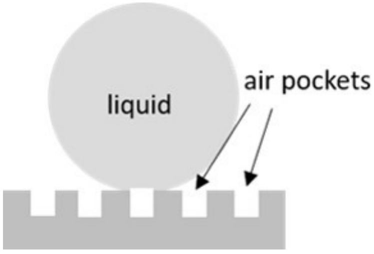

Figure 4. A spherical shape of water droplet with high contact angle on rough surface.

3. Environmental and human health concerns

Due to their chemical structure, PFAS are very resistant to decomposition and prone to accumulation, which as a sighnificant impact on the human health and the environment. Their persistence is causing air, water (including drinking water), soil and wildlife contamination. A major source of exposure is also household dust (Karaskova et al., 2016), which largly consists of short textile fibres. In addition, the long-range transport further contributes to their global distribution, as they have already been detected in the remote areas, i.e., in Arctic (Lin et al., 2020). People are therefore being exposed to PFAS through the environment, drinking water and food. PFAS have already been detected in human urine, breast milk and blood samples. Studies have also shown that the highest concentrations of PFAS in human blood have been detected are in the industrialised areas (Worley et al., 2017). Exposure to PFAS throught the skin, inhalation and ingestion has been associated with a wide range of adverse health effects, such as infertility, fetal development, thyroid hormone and kidney dysfunction, weakend immune system, reduced effectivness of vaccines, developmental problems in children and even cancer (Kleinman & Stevenson, 2021; Bil et al., 2023; Blake at al., 2018; Looker et al., 2014; EPA – United States Environmental Protection Agency, 2023). As a result, the health risks associated with PFAS have led to extensive regulatory controls and restrictions. Regulatory authorities around the world are taking steps to regulate the use, manufacture, and disposal of PFAS. In particular, the acceptable concentrations of certain PFAS compounds in water, soil and air have already been limited in the recent decades, in order to to restrict their release into the environment and reduce the associated risks. Restrictions have also been placed on the production and use of certain PFAS, such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). As a result, the industry, including the textile industry, is forced to look for PFAS-free alternatives to fulfil these regulations.

3. PFAS-free alternatives for the textile industry

3.1 Characheristics of ideal PFAS-free alternatives

Ideal PFAS-free alternatives for hydro-/oleophobic textile coatings should exhibit specific properties to ensure effective and long-lasting performance while addressing environmental and health concerns. These alternatives should have durable hydro-/oleophobic properties, that ensure the treated textiles effectively repel water and oil for multiple uses and wash cycles and withstand the exposure to sunlight, moisture and mechanical stress without compromising performance. Futhermore, in addition to ensuring the functional properties of the textiles, the durability of the coating contributes to the overall sustainability of the product by minimising the need for freequent reapplications. At the same time, the end-of-life aspect should also be considered when developing new coatings. These alternatives should also be versatile enough to be applied to a variety of fabrics without compromising their basic textile properties, i.e., breathability or flexibility. Furthermore, the PFAS-alternative coating should be cost-effective as this is particularly important to achieve a widespread industrial use. The alternatives should be economically viable for manufacturers, to make the transition financially feasible. The ideal alternative should not only offer competitive pricing, but also minimise production costs without compromising on performance, durability or safety. A balance between functionality, durability and sustainability is essential for the successful development and adoption of PFAS-free hydro-/oleophobic textile coatings.

3.2 Promising PFAS-free alternatives

Several promising PFAS-free alternatives are emerging as the textile industry searches for sustainable and environmentally friendly solutions. One promising research path involves the use of bio-based materials, such as biodegradable polymers from renewable sources. Natural polysaccharides, as well as oils and waxes from plants can be used to reduce the surface tension of the material and thus increase hydrophobicity. These alternatives not only provide an effective water and oil repellency but also, address concerns about persistence in the environment due to their bio-degradability. Another way to achieve hydro-/oleophobicity is to utilize the principle of increasing the surface roughness of the material, which can be achieved by using nanoscale materials. The use of nanoparticles allows precise control of coating thickness and uniformity and in addition to increasing the roughness of the textile fibres, can create a protective barrier between the fibre and water or oil. Moreover, additional functionality of the material can be achieved through the specific properties of the added nanoparticles, offering the potential to improve functionality and performance.

Several methods have been developed to produce superhydrophobic textiles using bio-derived compounds as low surface energy chemicals and/or nano/micro scale surface roughening components (Shahid et al., 2022). Two main approaches can be found in the literature. The first is a two-step application where the first step is surface roughening followed by superhydrophobisation (coating with low surface energy materials) and the second is a one-step coating or simultaneous surface roughening and superhydrophobisation.

In the first approach, the surface can be roughened by enzyme etching or coating with different nanostructures based on natural compounds such as chitosan, cellulose, lignin, bovine serum albumin and natural polyphenols. They all contribute to nanoroughening of textile surface before hydrophobisation with synthetic or natural low surface energy compounds. Materials used to create nano/micro scale surface roughness to textile include also TiO_2 (Xue et al, 2008; Kuruppu, 2021; Suryaprabha & Sethuraman, 2021), SiO_2 (Xue et al, 2008; Xue et al, 2009; Manatunga et al, 2016), ZnO (Fan et al, 2018; Gao et al, 2019; Lee et al. 2011; Ates & Unalan, 2012; Khosravi & Azizian, 2018), etc. Coating of nanostructures can be done by various methods, e.g., dip coating, solution immersion, dip-pad-dry-cure, spray coating, spin-coating, in-situ growth, etc. There are several biomaterials that have been used for lowering surface energy. Among them, fatty acids and their salts, for example stearic acid (Xue et al., 2008; Lee et al., 2011, Richard et al., 2013; Pan et al., 2012; Li & Guo, 2017; Suryaprabha & Sethuraman, 2017; Dong et al., 2019; Kundu et al., 2019), sodium stearate (Teli & Annaldewar, 2017; Lu et al., 2018), zinc stearate (Lu et al., 2018), copper stearate (Pan et al., 2019), calcium stearate, lauric acid (Fan et al., 2018), sodium laurate (Pan et al., 201; Liu et al., 2015), ammonium palmitate, cinnamic acid and myristic acid have been preferred. Other materials that have been used are natural waxes such as beewax or carnauba wax, cellulose oleoyl ester and cardanol- and eugenol- based benzoxazines (Shahid et al., 2022). The second step (low energy treatment) is usually carried out by dip coating or dip-pad-dry-cure (Shahid et al., 2022).

The second procedure is coating the textile substrates with pre-hydrophobised nanostructures (Shome et al., 2019; Gu et al., 2019; Rahman et al., 2021; Ivanova & Philipchenko, 2012). Compared to the first procedure this one takes less time, potentially costs less and is easier to apply in large scale applications. Bio-based superhydrophobic formulations that have been used until now contain cellulose oleoyl ester nanoparticles (Xiong et al., 2017), nano lauric acid copper (Zhang et al, 2019), beewax/lignin (Zhang et al., 2020), cationic starch/carnauba wax (Forsman et al., 2020), cellulose nanocrystals/chitin nanocrystals/chitosan (Yagoub et al., 2019), PLA/nanoclay (Gore & Kandasubramanian 2018), Chitosan/TiO_2 (Ren et al, 2020), cinnamic acid/myristic acid functionalised sepiolite nanoparticles (Razavi et al., 2019), etc. Among the various coating techniques employed, dip coating and spray coating are most widely used.

Most research achievements in the filed of bio-based production of hydrophobic textiles are still limited to laboratory-scale trials. Due to their low durability, the lack of standardised protocols and the lack of operational complexity, the processes described are not yet suitable for mass production. One of the most important remaining issues is how to develop long lasting hydrophobic textiles using biomaterial-based methods with well-defined procedures to meet the urgent market demand.

4. Current challenges and future perspective in the PFAS-free coating development

The search for PFAS-free alternatives for textile coatings is currently facing several challenges. A key challenge is the technical complexity of developing alternatives that match the performance characteristics of conventional PFAS coatings. Achieving a comparable level of functionality without compromising durability remains a major obstacle. Developing alternatives that match or exceed the performance of PFAS in water and oil repellency while maintaining durability is a complex task. Another technical challenge isto take into account the wide range of substrates and fabrics used in the textile industry, as PFAS-free alternatives must be compatible with different materials. Another challenge is to ensure that these alternatives remain effective after multiple wash cycles and environmental conditions during wearing. In addition to closing the performance gap, it is particularly important for the textile industry to ensure a manufacturing process that is economically viable and suitable for mass production. Overcoming these multiple challenges will require interdisciplinary collaboration between researchers, manufacturers, regulators and markets to drive innovation, improve performance and facilitate the widespread adoption of PFAS-free alternatives in the textile industry.

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Conflicts of Interest: The authors declare no conflict of interest.

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