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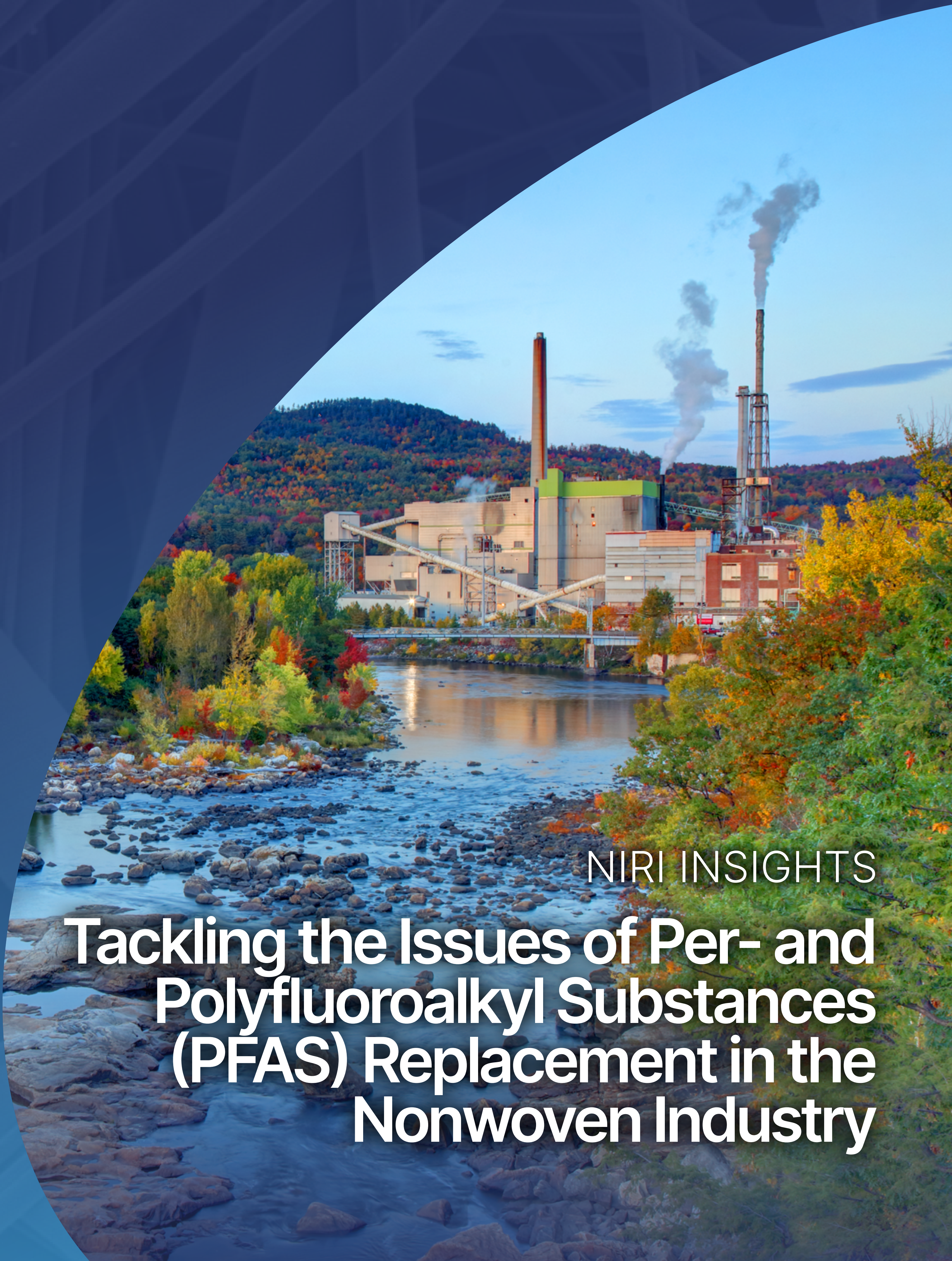


NIRI INSIGHTS

Tackling the Issues of Per- and Polyfluoroalkyl Substances (PFAS) Replacement in the Nonwoven Industry

CONTENTS

Explore the urgent need for PFAS replacement within nonwoven and fibre based products and where opportunities exist to achieve this through innovations in nonwoven and materials science.

INTRODUCTION

From single use hygiene products to durable, long-life, nonwoven fabrics, regulations and legislation are continuing to shape environmental and social responsibility policies and helping to drive the development of more sustainable materials, manufacturing processes and finished products, across multiple market sectors.

The nonwovens and textile industry has responded impressively to recent EU sustainability regulations and strategies concerned with single use plastics and circularity by upgrading product designs, increasing recycled, natural, and biobased polymer content, and accelerating the implementation of new recycling technologies.

Now with new EU PFAS regulations on the horizon our industry is faced with another pressing need to innovate

These new regulations, which are scheduled to come into effect in 2025, will restrict the use of Per- and polyfluoroalkyl substances (PFAS) and will affect a large variety of nonwoven and textile products, ranging from filter media, to building and construction fabrics. The restrictions will add to those already imposed by the EU, the U.S. Environmental Protection Agency (EPA) and by individual US states including California, New York and Washington.

Often termed 'forever chemicals' due to their persistent, non-degradable nature PFAS chemicals have been found to contaminate water sources, disrupt ecosystems, and pose risks to human health

Shaping a future without PFAS

Exactly how PFAS will be regulated is still in a state of flux and will be influenced on both sides by industry bodies and environmental organisations. However, what is clear is that the nonwoven industry's unconstrained use of PFAS is neither sustainable nor conscionable given the growing scientific consensus on the environmental and human health threats posed by PFAS.

This short report provides readers looking to understand and tackle the issue of PFAS replacement across a diverse range of markets including filtration, transport, construction, medical and protective clothing, with an introductory insight into how new material science and fibre innovation, coupled with pragmatic product design decisions, can provide opportunities to reduce dependency on PFAS without compromising basic performance requirements.

THE PROBLEM WITH PFAS

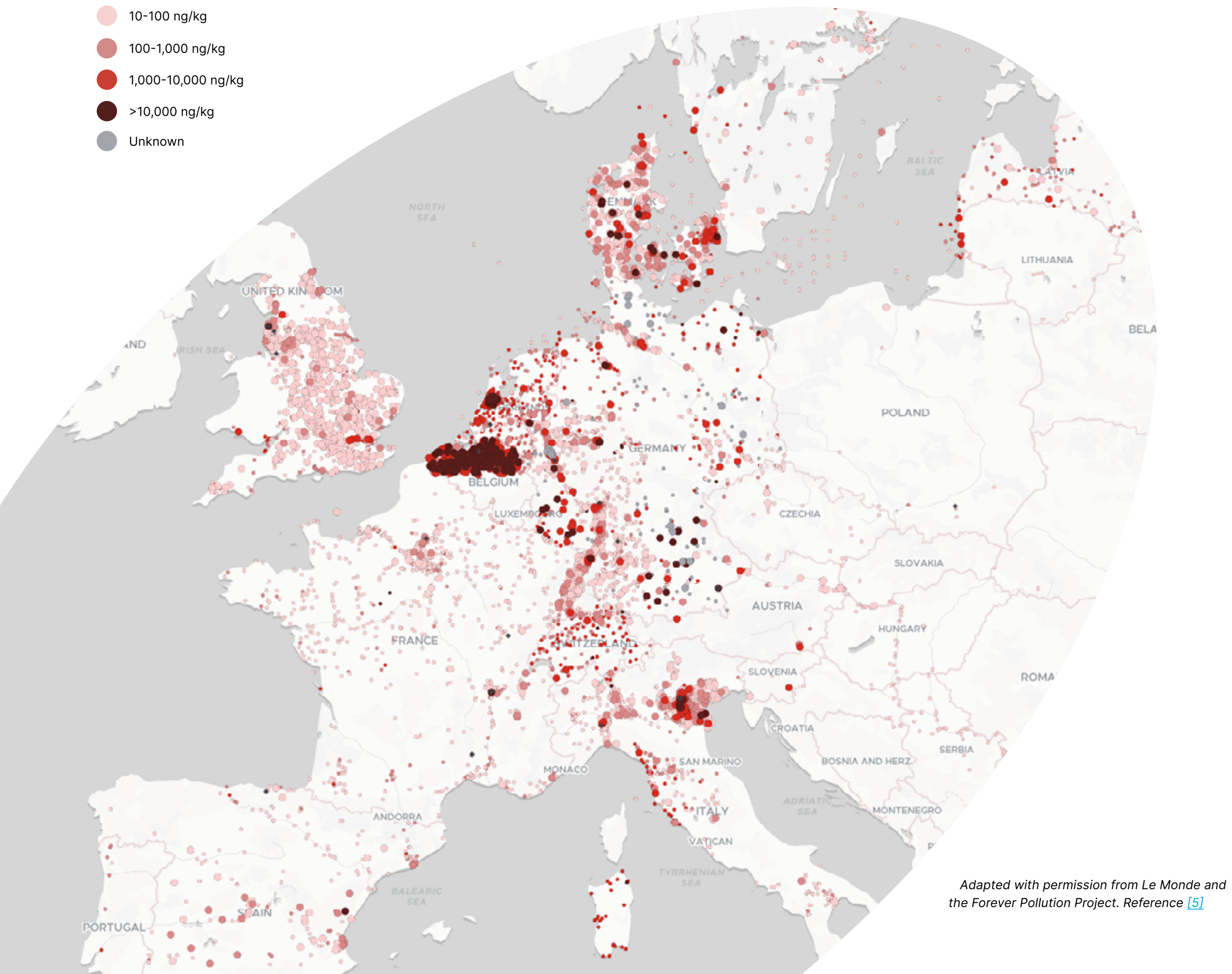
PFAS is an umbrella term for per- and polyfluoroalkyl substances; a group of synthetic 'forever chemicals' used extensively in many industries, including the European textile and nonwoven industries, which consume over 90,000 tonnes per annum. [1] In the US, the Environmental Working Group (EWG) has identified over 1,500 textile mills which it deems are likely releasers of PFAS chemicals into the environment. [2]

Properties and persistence

PFAS possess a valuable combination of properties including thermal and chemical stability, as well as exceptional oil and water repellency, which along with excellent process compatibility and functionality at low addition levels, has led to their widespread use across numerous products, from filter media, to waterproof and stain resistant fabrics.

The unique carbon-fluorine bond chemistry of PFAS, which is responsible for their chemical stability and widespread industrial value (Figure 2), also confers remarkable resistance to enzymatic and other known degradation pathways. Consequently, the ability of PFAS to persist in the environment following unintended leakage, has led to their long-term environmental accumulation, contaminating soil, ground, and surface water.

Figure 1 | Distribution of PFAS Contamination in Europe



Adapted with permission from Le Monde and the Forever Pollution Project. Reference [5]

Environmental distribution and health effects

Given the extensive geographic distribution and environmental accumulation of PFAS, it is unsurprising that human health concerns have emerged due to contamination of water supplies and the food chain. Although initially believed to be inert with uncertain effects, the propensity of PFAS to bioaccumulate in the body has since been linked to several chronic diseases, and as well as to reduced fertility.

Substantive evidence has emerged of links between exposure and health biomarkers associated with disease of the kidney, liver, bowel, and thyroid, specifically cancer. [3] Negative effects on hormone regulation is another concern. [4] Exposure has also been linked with acute health conditions such as high cholesterol, placing individuals at higher risk of stroke or heart attack.

Environmental PFAS contamination is now widely distributed across Europe, as well as globally (Figure 1). [5]

The challenge posed to the nonwovens industry

Unconstrained industrial exploitation of PFAS is not sustainable nor societally acceptable, and industry is faced with major challenges as access to PFAS chemistries becomes

Companies are now being challenged to explore what options are available to reduce or eliminate their dependency on PFAS whilst still maintaining product performance

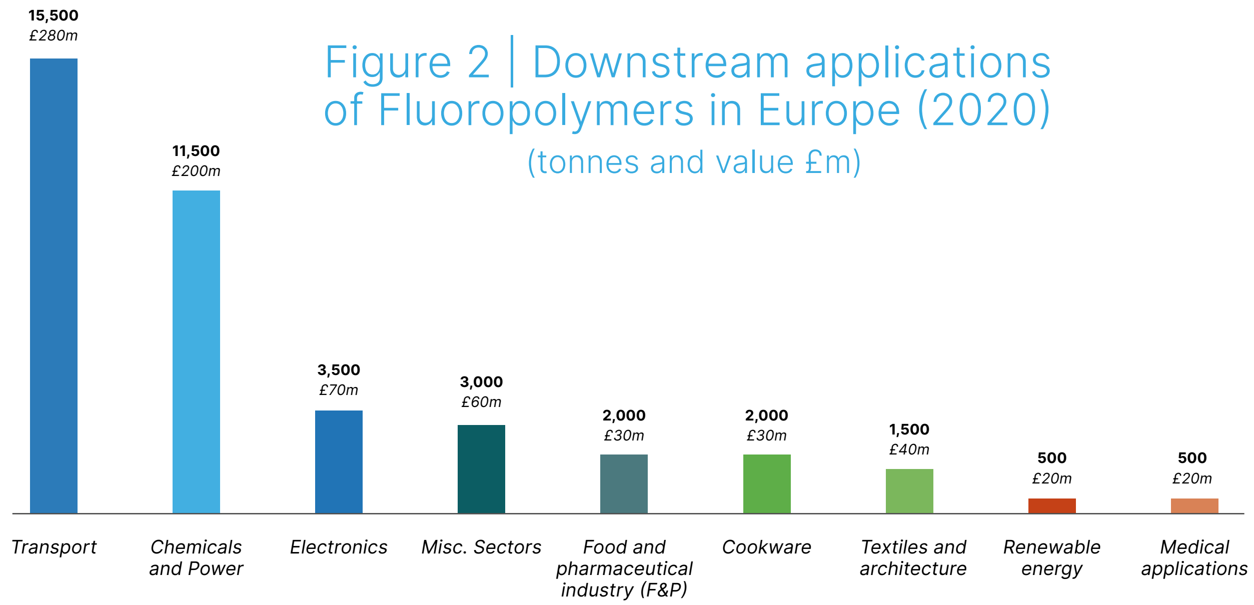
increasingly restricted. In 2022, multi-national companies again expressed their commitment to exiting PFAS production by the end of 2025. [7] A move reflected by many other major players in the chemicals industry who are moving away from PFAS use across most manufacturing processes.

At NIRI we have already seen how this transition is impacting the availability of PFAS additives to manufacturers and converters in the nonwoven sector, resulting in some companies needing to restrict their use of existing stocks of PFAS and focus use on a smaller number of products, a reallocation that has left some products out of specification and underperforming.

The urgency to find PFAS-free approaches cannot be underestimated, especially given the timelines associated with EU and US regulation covering the manufacturing, use and environmental release of PFAS.

Figure 2 | Downstream applications of Fluoropolymers in Europe (2020)

(tonnes and value £m)



Drawn from Figure 3.1 of reference [6]

THE REGULATORY LANDSCAPE

At the beginning of 2023, two new pieces of EU legislation came into force which limit human exposure to harmful quantities of PFAS. The concentrations of PFAS compounds in food are now regulated by Commission Regulation (EU) 2022/2388, while Directive (EU) 2020/2184 places limits on the presence of PFAS in drinking water.

In parallel to these EU regulations, the EPA has introduced a range of strategies and programmes to limit human and environmental exposure to PFAS, including removal of an exemption permitting organisations to avoid reporting the release of small quantities of PFAS to the environment. [8] The EPA has also proposed a rule that would prevent commencement or resumption of the manufacture, processing, or use of three hundred or more dormant PFAS chemicals that have not been made or used for many years, without a complete review and risk assessment by the EPA. [9][10]

Restriction of PFAS in end-use products

Another significant date on the regulatory horizon is 2025, when The European Chemicals Agency (ECHA)'s recommendations on the restriction of PFAS chemicals will pass into law and become part of REACH regulations. This will result in a total ban on the use of many PFAS above a threshold quantity at the end of a limited 18-month transition period.

Certain derogations to the law will be permitted based on socio-economic considerations and the availability of

alternatives, although these will gradually cease over the next 5 and 12 years. In addition, some time-unlimited derogations are proposed, such as for example, PFAS used as active substances in plant protection products, biocidal products, and human and veterinary medicinal products. [11]

PFAS vs Fluoropolymer

Many players within the chemical industry and industrial sector are seeking to differentiate fluoropolymers from PFAS chemicals. Whilst a key chemical manufacturer has announced its exit from food contact and cosmetic use of PFAS, as well as a transition away from the use of fluorinated surfactants in the synthesis of fluorinated polymers, they are strongly against the banning or restriction of fluorinated polymers themselves. [12] This position is mirrored by other major players in fluoropolymer manufacture. [13]

The nonwoven industry will need to wait for the decision from the ECHA on how fluorinated polymers may be restricted, but due to uncertainties around their disposal at end of life it seems unlikely that they will escape EU regulation entirely

Fluoropolymer foams find application in aerospace interiors and seating due to their low flammability and low smoke release. Fluoropolymers are used throughout the aerospace industry.

KEY REGULATORY DATES IN THE EU

2009

International/Stockholm Convention

Stockholm Convention of persistent organic pollutants updated to include Perfluorooctane sulfonic acid (PFOS). Effectively controlling production and distribution to specific applications.

2019

International/Stockholm Convention

Stockholm Convention of persistent organic pollutants updated to include Perfluorooctanoic acid (PFOA) to control production and distribution to specific applications.

JUN2022

International/Stockholm Convention

Stockholm Convention on persistent organic pollutants updated to ban the production and distribution of Per-fluorohexane sulfonic acid (PFHxS) entirely

JAN2023

Denmark, Germany, Netherlands, Norway, and Sweden

A proposal to introduce a class chemical ban affecting the production and distribution of >10,000 substances (based on elements of their structure) is submitted to EU member states for consultation.

FEB2023

EU/REACH

C9-C14 perfluorinated carboxylic acids (PFCAs) entered the REACH candidate list of substances of very high concern (SVHC).

MAR2023

EU/REACH

Start of ECHA Consultation Period.

SEP2023

EU/REACH

ECHA Committees' evaluation began.

2025

EU/REACH

Proposed Legislation enters law and EU member states adopt the ECHA recommendations. An 18-month transition period begins.

2026/27

EU/REACH

Proposed 18 Month transition period ends.

2030/31

EU/REACH

Proposed 5 Year derogation for food contact products ceases.

2037/38

EU/REACH

Proposed 12 Year derogation for medical devices ceases.

HOW CAN THE NONWOVEN INDUSTRY RESPOND?

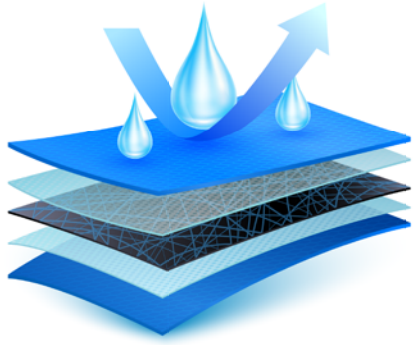
Not all products are created equal

As acknowledged by the EU 5- and 12-year derogations, not all products will face the same level of challenge in their PFAS replacement journey.

This is equally true in nonwoven applications where performance requirements will differ greatly from product to product. Certain applications place the most stringent requirements on nonwoven product performance, such as in Chemical, Biological, Radiological and Nuclear (CBRN) products, filter media and protective clothing, where the degree of thermal stability and chemical resistance required are not easily met by alternative PFAS-free chemistries.

The low cost and ubiquitous nature of PFAS means that these chemicals have also found their way into a large range of products where alternative chemistries, or other PFAS-free approaches, could be effectively harnessed to address product performance

Single use food packaging is a prime example of where PFAS can be replaced with more environmentally friendly options. However, the same applies to many other nonwoven and textile products, such as some found in the construction, filtration, hygiene, and medical sectors, where a careful re-evaluation of how these products are designed and formulated may help to reduce their demand on PFAS or eliminate the need for them entirely.



Layered nonwoven constructions can be designed to minimise the impact of oils, water and chemicals on the performance of the product.

How can we influence the bulk performance of the product through intelligent nonwoven design?

A pragmatic approach to PFAS replacement

An alternative approach to depending solely on a thin surface coating to provide product performance is to ask how we can manage the interaction of water, oils, and other contaminants within the nonwoven structure itself and prevent strikethrough or appearance change on the surface.

This approach has already been harnessed by NIRI to evaluate with customers how to effectively navigate the transition away from PFAS chemicals whilst achieving necessary product performance. The approach looks to exploit innovations in fibre science, as well as alternative nonwoven fabric constructions and membranes, which when assembled appropriately - especially in laminated or layered fabric constructions – can be capable of reducing the need for PFAS additives. For example, the addition of functional meltblown, spunbond or electrospun layers to an existing product, or the introduction of layers containing appropriate fibre blends presents opportunities to strike the necessary balance between permeability and the required oil and water repellency.

No time to wait for a magic bullet

For years, strategies targeting the development of universal chemistries capable of substituting PFAS to deliver equivalent performance, akin to a 'magic bullet' have fallen short. There is no imminent prospect of a PFAS-free analogue chemistry capable of replicating the same combination of properties and attractive economics.

A one size fits all solution suitable for industrial use across all nonwoven and textile products is unrealistic, especially given how close regulatory deadlines are on the horizon

It is therefore important to have clarity about the specific performance criteria that is currently necessitating the use of PFAS in a specific textile product. Reconsidering the product specifications by de-coupling all the combined requirements can also help rationalise the use of hydrophobic and oleophobic coatings. Water resistance, oil resistance, stain resistance and alcohol repellency are quite separate issues, and can be addressed to varying extents using PFAS-free approaches.

Incorporating circular economy approaches

The opportunity to redesign nonwoven and textile products for PFAS replacement also presents an opportunity to ensure any new developments are compatible with circular economy approaches and to mitigate concerns about the leakage of ecotoxic chemical compounds and plastics into the environment. To ensure product designs are sustainable and future proof, it is important to consider all chemical and material selection choices, as well as plausible reuse and recycling strategies at the design stage. This is an opportunity to re-evaluate and upgrade product designs, which in some cases haven't significantly evolved in the decades that PFAS has been available.

Addressing overspecification

More broadly, there is also scope, in some specific cases, for an industry-wide review of the technical specifications and standards to which certain products are tested. For example, standards relating to water repellency for certain consumer products can tend to be over-specified given real-world use cases. Such reviews would require a concerted effort from key industry players and close engagement with regulatory and testing bodies, but such an initiative could ultimately help to eliminate the need for PFAS in a variety of existing applications.

ENGINEERING FIBRE SURFACES TO HELP WITH PFAS REPLACEMENT

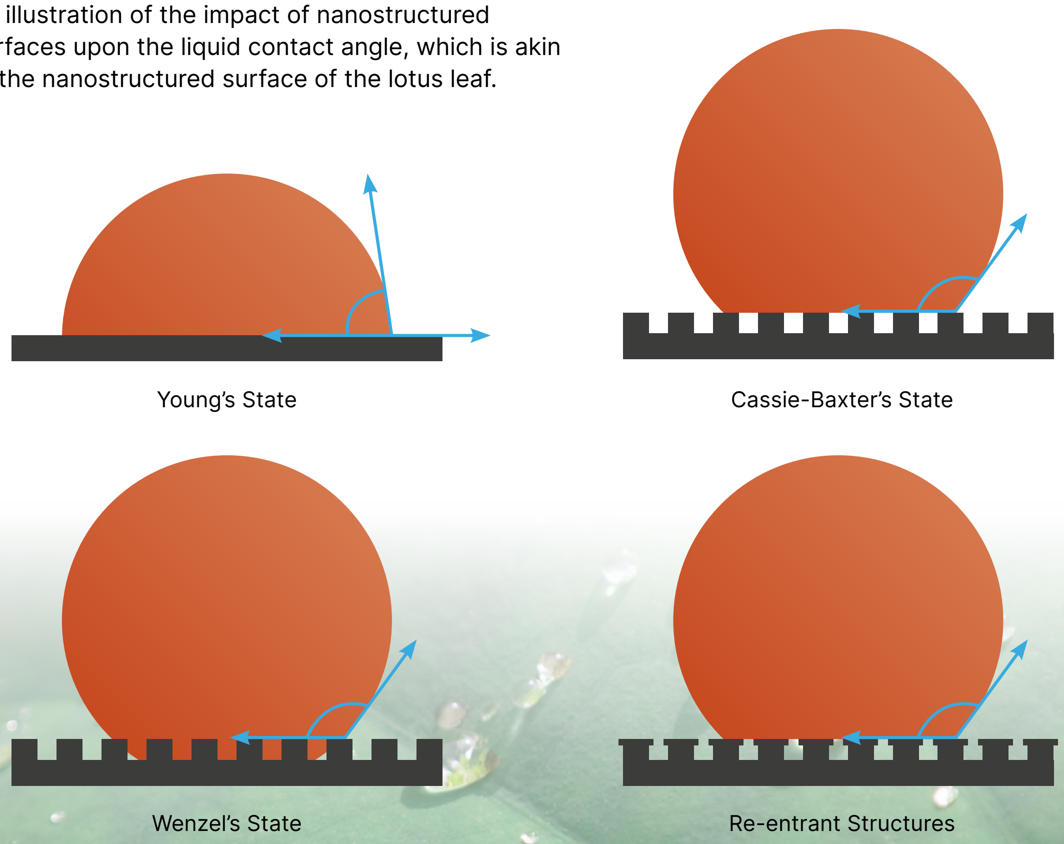
Finding a substitute chemistry that is capable of directly replacing PFAS additives without any performance compromises, remains highly elusive and is no trivial task. Despite the technical challenges and remaining performance gaps, some progress has been made in producing commercially available, or scalable PFAS-free formulations offering attractive levels of performance.

Fluorine-free durable water repellents (hydrophobic treatments) include, but are not limited to those produced by Archroma, CHT, Daikin, Huntsman, Teflon, Rudolf, Green Theme Technologies, Beyond Surface Technologies, OSM shield and Lamoral coatings. Many brands within the performance clothing and home textile and furnishings sectors have already switched from PFAS to alternative water repellent treatments for many products. However, PFAS use remains common practice.

Whilst water repellency can be delivered by several alternative chemistries relatively well, the challenges of oil repellency and stain resistance are much greater due to the low surface tension of oils. This challenge is also illustrated in nature, where fewer oleophobic surfaces exist than hydrophobic [14]. Meaning industrial approaches based on biomimicry, such as the lotus leaf effect [15] to provide oleophobic properties are more limited than those directed at hydrophobicity.

Figure 3 | Classical Liquid Droplet Wetting Behaviour

An illustration of the impact of nanostructured surfaces upon the liquid contact angle, which is akin to the nanostructured surface of the lotus leaf.



Note: Illustration of the classical liquid droplet wetting behaviour model redrawn from reference [18]

Table 1 | Summary of PFAS-Free Alternative Chemistries and Materials

PFAS Alternative Chemistry	Function	Potential Hazards
Silicones/siloxanes		While Polydimethylsiloxane (PDMS or dimethicone) is generally considered inert and without adverse effects, it can contain cyclic siloxane impurities known as D4 and D5 that are persistent and bioaccumulative.
Silanes		Some silanes used to treat textiles such as chlorotrimethylsilane are persistent, mobile, and toxic. Dimethoxydimethylsilane is a reproductive and chronic toxicant.
Paraffin waxes/ hydrocarbons		Aquatic chronic toxicity of C9-C14 Isoparaffins.
Fatty acid derivatives		Relatively low hazard materials.
Melamine and melamine formaldehyde coatings		Melamine is listed as an International Agency for Research on Cancer (IARC) group 2B carcinogen (potentially carcinogenic to humans) and may cause damage to the kidney and bladder. Formaldehyde is on the US Department of Toxic Substances Control's (DTSC) Candidate Chemical List, citing carcinogenicity, hepatotoxicity, digestive system toxicity, ocular toxicity, and respiratory toxicity.
Polyurethane coatings		Hazards are mostly associated with monomers used in the manufacture of polyurethanes. Polymer forms such as polyurethane emulsions present lower risk.
Acrylates/Acrylic Polymers		Hazards are mostly associated with monomers used in the manufacture of acrylic polymers. Polymer forms such as acrylic polymer emulsions present lower risk.
Dendrimers		Hazard traits are based on individual components of specific dendrimer formulations (e.g., organic silicon compound, organic acid, acetic acid, functionalised polymer, cationic surfactant, hydrophilic group, crosslinker).
Silicon dioxide nanoparticles		Potential neurotoxicity and genotoxicity.
Titanium dioxide (TiO_2) nanoparticles		TiO_2 (airborne, unbound particles of respirable size) is on DTSC's Candidate Chemical List because it is on the Prop 65 list as a carcinogen and on the International Agency for Research on Cancer (IARC) Carcinogen list 2B (possible carcinogenic to humans). TiO_2 is also persistent and can release metal ions into the environment.

Water repellency
Soil repellency
Stain repellency
Oil repellency

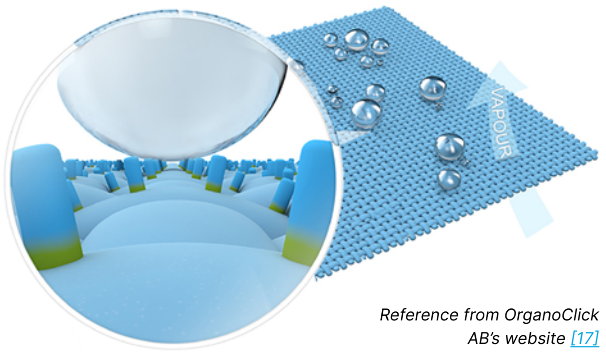
Note: Potential Hazards listed are taken from the DTSC's potential alternatives to perfluoroalkyl and polyfluoroalkyl substances (PFAS) in treatments for converted textiles or leathers. [16]

Decreasing the wettability of surfaces often relies on the application of low surface energy or hydrophobic coatings, such as those outlined in Table 1, to the surface of fibres. However, in the case of nanoparticle treatments and dendrimer chemistries (see Figure 4), these treatments can also impart physical surface modifications such as changes in surface roughness that can help modulate hydrophobicity and/or oleophobicity of the surfaces, manifested by a change in the droplet contact angle akin to the lotus leaf effect. The influence of nanoscale surface structures on contact angle is demonstrated in the classical liquid wetting models shown in Figure 3. [18]

In addition to surface coating treatments there are also attractive opportunities to directly modify the surface roughness of fibres themselves for example by changing the surface morphology of fibres during production, or postproduction through fibrillation and etching, or by the attachment of inorganic particles to fibre surfaces (see Figure 5 [19]). Such fibre surface chemistry modifications have already attracted much attention and represent a significant opportunity to enhance the performance of nonwoven products against oil, water, alcohol and stains.

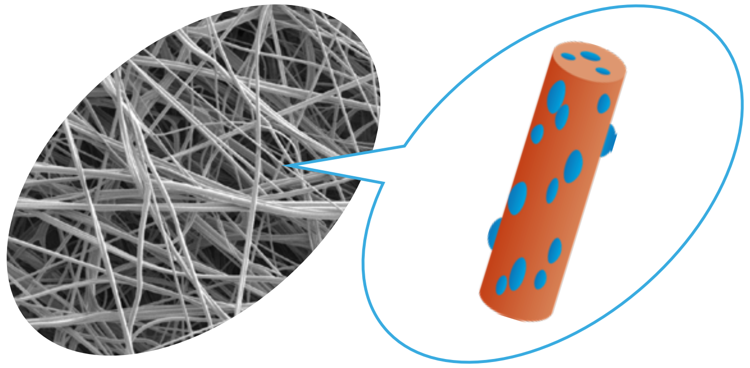
There is no one route to PFAS replacement, but by fundamentally reappraising the design of existing nonwoven products that currently rely on PFAS additives, and by harnessing PFAS-free functional coatings coupled with intelligent nonwoven fabric design, it is often possible to meet key performance requirements using an entirely PFAS-free approach

Figure 4 | Demonstration of OrganoClick AB's Dendrimer Oragnotex technology



Reference from OrganoClick AB's website [17]

Figure 5 | An illustration of fibres generated in-situ with nanoscale features, for example by electrospinning



Redrawn from reference [19]

Reducing energy usage whilst retaining nonwoven performance

Wet chemistry and coating techniques, although effective and highly scalable, often require energy intensive drying steps and in some instances can be detrimental to the filtration performance, air permeability or other physical properties such as fabric stiffness and handle. One interesting technique currently being evaluated by NIRI is in-line plasma and chemical vapour deposition (CVD) techniques to introduce the types of dendrimer and patterned surface structures (illustrated in Figures 4 and 5) on fibre surfaces to impart liquid repellency.

SUMMARY AND WHERE TO NEXT

Navigating the transition to a PFAS-free nonwoven and textile product landscape, and being ready for the impending regulatory changes, requires collaboration between industry and external R&D partners to accelerate innovation that is targeted at delivering performance on a product-by-product basis.

In some specific cases, the technical need for PFAS in certain nonwoven and textile products is questionable and could be revaluated, especially where it can be shown performance is over-specified given the real-world functionality required.

In other product applications, where use of PFAS is entirely rational, there are opportunities to explore its removal, by harnessing new material and fibre science developments and surface functionalisation techniques, in conjunction with upgraded or modified fabric constructions to modulate bulk performance in other ways, instead of relying on a surface coating.

Now is also an opportunity to take account of growing consumer awareness of sustainability and social responsibility, by responding to the PFAS-free challenge ahead of the EU legislative deadlines to deliver premium brand positioning and to increase market share. Manufacturers and converters involved in global distribution of products containing PFAS chemicals perhaps face the greatest challenge, and there is now a race against time to develop and bring to market alternative, innovative products that continue to meet consumer requirements.

Harnessing innovation ahead of EU legislative deadlines can position brands at the forefront of sustainability, delivering premium value and capturing greater market share in a PFAS-free future

TACKLING THE TRANSITION TO PFAS-FREE PRODUCTS

By supporting companies across the full nonwovens and textile supply chain, NIRI has been immersed in the challenges being faced by our industry in eliminating PFAS chemicals from products. Our mission is to support organisations in delivering step-change sustainable innovation across every sector of the nonwoven and textile supply chain including automotive, construction, hygiene, filtration, and apparel.

Implementing change can be challenging but NIRI is fully engaged and invested in supporting the nonwovens and chemicals industry to tackle the imminent challenges of PFAS replacement. Our experts and world-leading prototyping facilities are on hand to help companies navigate the complex transition to PFAS-free products and we are uniquely positioned to provide organisations with bespoke guidance on how to navigate PFAS issues.

NIRI is on hand to support your business with:

- Strategies to redesign products to reduce their need for PFAS
- Approaches to match product performance and efficacy without PFAS
- The sourcing of PFAS-free alternative products and components
- The development and prototyping of PFAS-free products
- The synthesis of PFAS-free coatings and repellent treatments
- The treatment of fibres and nonwovens with PFAS-free chemistries
- The testing and validation of product performance
- Support in the commercial implementation of PFAS-free approaches

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ABOUT NIRI

NIRI is a world-class innovation and product development supplier of sustainable materials, fibres, nonwovens, and their associated products. With industry leading expertise and full prototyping and analytical capability, our business is designed to accelerate innovation, develop commercially viable products, identify new market opportunities and provide world-class scientific advisory services.

Having completed over 900 projects for over 450 customers across the whole of the nonwoven supply chain, our rapid growth as an organisation is mirrored by the value and growth we provide to our customers.

For more information, or to discuss how this approach could fit your business, please contact:

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