Greener Solutions Case Study: Alternatives to Per- and Poly-Fluoroalkyl Substances in Aftermarket Carpet Treatments

What was the Challenge:

Per-and polyfluoroalkyl substances (PFASs) are commonly used as water and stain repellent agents on fabrics, furniture, and carpets (1). These products are generally purchased by consumers and directly applied to home carpets in a spray or aerosol form, in contrast with agents that are applied during manufacturing and prior to installation (1). PFASs used in carpet manufacture are known to cause a variety of health hazards and were identified by the California Department of Toxic Substances Control (DTSC) as a priority product in 2021 (2). While certain PFASs had already been voluntarily phased out in carpet manufacture since 2008 (3), their use in aftermarket treatments remains a large segment of products featuring fluorinated active ingredients, with little data on the compounds present in the formulations. In order to facilitate proactive and cooperative change to industry, priority product designations are supported with a DTSC mandate to investigate safer alternatives. The research presented in this case study is the result of collaboration between DTSC and the student team from UC Berkeley's Greener Solutions course.

The team was tasked with performing a chemical hazard and technical performance assessment of both existing PFAS-containing products and potential alternatives. The team identified Scotchgard™ as the baseline of comparison due to its widespread use and name recognition as a surface treatment for stain repellency (1). The product was formulated with perfluorooctanesulfonic acid (PFOS) up until 2003, when it was reformulated in response to calls to phase out the material (1). However, PFOS was simply replaced with another proprietary PFAS mixture, likely containing perfluorobutanesulfonic acid (PFBS) and 6:2 fluorotelomer alcohol (6:2 FTOH)(4). These two compounds served as the chemical baseline for measuring both the environmental health and safety (EH&S) and technical performance of the alternatives. While numerous textile protectants that claim to be fluorine-free are already on the market, their compositions are not publicly available and therefore cannot be assessed for chemical hazard.

The team focused their investigation on alternatives that:

1. Can be applied in the form of a liquid spray or aerosol formulation
2. Provide overall carpet protection rather than spot treatments
3. Are hydrophobic to protect against a broader range of stains, such as beverage spills and pet accidents
4. Demonstrate improved EH&S performance from the baseline, with special attention placed on skin irritation potential and respiratory irritation due to the alternatives' intended aerosol application

To assess overall technical suitability in comparison with Scotchgard™, the team selected the following metrics: contact angle for both hydro- and oleophobicity, wash cycle resistance for washability, and sustainability and sourcing. To assess EH&S performance, the team chose the following health endpoints: carcinogenicity/mutagenicity, developmental/reproductive toxicity, skin/eye irritation, aquatic toxicity, persistence/bioaccumulation, and endocrine activity.

Several promising alternatives to PFASs in aftermarket treatments were then selected by the team and categorized into strategies based on similarities in material properties. The strategies included biopolymers and silicon-based materials. In both technical and EH&S categories, scores were assigned to each alternative on a "scorecard" which allowed for comparison with the baseline as well as across alternatives.

At the conclusion of the project, the team recommended the combination of chitosan with silicon dioxide nanoparticles (SiNPs) as the most promising strategy to pursue. The compound strategy takes advantage of the complementary strengths of both materials, and is potentially capable of repelling both water- and oil-based stains, while introducing anti-microbial properties not seen in existing PFAS treatments.

Why this Project was Important:

The Department of Toxic Substances Control's October 2019 report, *Proposed Priority Product: Treatments Containing Perfluoroalkyl or Polyfluoroalkyl Substances for Use on Converted Textiles or Leathers*, identified PFASs used in treatments for carpets and other fabrics as a potential priority product and signaled an increase in regulatory attention toward the health impacts of PFASs (5). A priority product designation indicates that a consumer product identified by the DTSC contains one or more chemicals that have a hazard trait that can harm people or the environment (6). As part of the priority products program, the DTSC aims to facilitate voluntary phase-out of harmful materials by collaborating with affected industries to identify safer potential alternatives. BCGC's Greener Solutions course helps bridge the gap between industry and regulatory stakeholders by conducting research into alternatives that consider industry needs such as technical performance and economic feasibility alongside regulatory needs such as human and environmental health hazards.

The most common PFAS compounds used for aftermarket treatments for carpets are fluorinated polymers (5). Toxicity and bioaccumulation potential of these polymers are not well documented, but one strategy for assessing hazard levels of these compounds is to assess their monomers instead. While monomers often cannot be directly compared to the hazards and performance of their polymer forms, they still provide useful information where there otherwise may not be any available. For example, monomers are an important consideration in this context due to their potential to release into the environment during the production process, persistence as an impurity in the final product, and as a result of polymer degradation (7). This evaluation strategy was applied for the analysis of fluorinated polymers outlined in this report.

From the industry needs perspective, consumer demand for safer alternatives to PFASs is also rapidly rising due to widespread negative reports on the health effects of fluorinated barrier materials, such as in food packaging. In response, a number of non-fluorinated textile protectant formulations such as Teflon EcoElite, Trinova and Vectra have been released, but these products cannot be assumed to be safe, since their exact compositions remain an industry secret. Finding alternatives to PFASs in the aftermarket treatment industry is a complex and multi-layered challenge due to competing market demands for highly functional chemicals that often over-perform and benign products with low hazard-- transparent product formulations are especially critical to prevent regrettable substitutes.

Who was Involved:

This project was initiated by the Berkeley Center for Green Chemistry as part of Greener Solutions, a project-based graduate level class offered through the School of Public Health. Interdisciplinary teams from the course offer green chemistry solutions to problems posed by industry. The team dedicated to researching alternatives to PFASs for use in aftermarket carpet treatments was mentored by Simona Balan of the California Department of Toxic Substances Control (DTSC).

The team consisted of five UC Berkeley Students: Amanda Bischoff, a PhD candidate in the Chemical Biology Program, Zhenya Chen, a second year Master of Public Health student, studying Environmental Health Science, Nancy Gutierrez, a Master of Public Health candidate in the School of Public Health, Samantha Vega, a graduate student pursuing a Master of Public Health in Environmental Health Science with an emphasis in Industrial Hygiene, and Emily McGauley, a third year undergraduate student majoring in Molecular and Environmental Biology.

What were the Proposed Solutions:

Strategy 1: Biopolymers

Biopolymers are a class of materials that can offer the technical performance of polymers (flexibility, durability, etc.) but are able to be sustainably sourced and produced from waste material, fungi, or plants (9). Chitosan and cellulose nanocrystals (CNC) were chosen as representatives from the broader class of biopolymer materials, as they both present promising textile protection properties. The team was inspired to look at bio-sourced materials as an opportunity to identify new applications for waste products in the case of chitosan, and to take inspiration from the use of cellulose by plants to form sturdy cell walls.

Chitosan

Chitosan is an abundant biopolymer (most commonly sourced from crustacean shell waste and the cell walls of fungi) which exhibits hydrophobic properties as well as antimicrobial properties (10). As a cationic polymer, it is able to be solubilized in acidic environments, allowing it to be applied in aerosol or spray form (9). The necessary acidic environment can be achieved using safe solvents such as dilute acetic acid. Additionally, chitosan is already being used in a commercial textile protection product, Tidal-Text^{TM} by Tidal-Vision, which makes an analogous carpet treatment product very promising (11). Furthermore, the structure of chitosan exhibits several opportunities for the material to hydrogen bond with nylon carpet fibers in order to form a barrier coating (12). Chitosan also shows a potential to hydrogen bond with water-based stains, thereby binding the compounds and acting as a barrier to prevent the stain compounds' absorption into the nylon fibers.

Chitosan also exhibits additional features which make it a promising carpet additive. The material has been shown to have antimicrobial properties by disturbing the cell walls of microbes and causing proteins to degrade, thereby acting as a cleaning agent for textiles (13). Chitosan-based dyes have also been shown to self-repair and heal microscopic cracks and broken bonds (14). The combination of these properties show potential for an aftermarket carpet treatment product that not only protects fibers from spills, but also reduces microbial activity and self-heals damaged fibers, leading to a highly versatile product that offers protection against chemical, biological, and mechanical sources for wear.

Overall, chitosan is an abundant and sustainably sourced biopolymer that is already being used in related textile treatment applications, which suggest a highly feasible shift to use on carpets. Its reported antimicrobial and self-healing properties even suggest added value as a carpet treatment over what is currently offered by PFAS-based products.

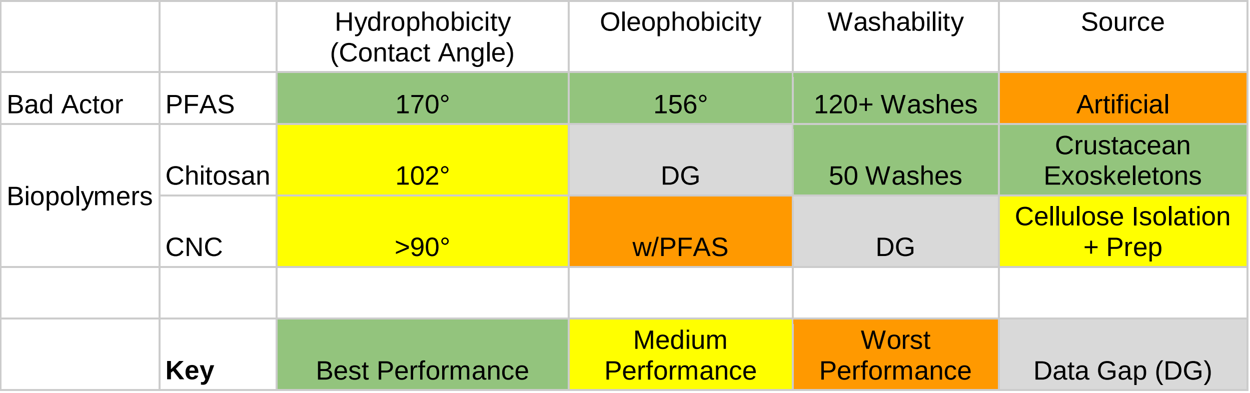
Cellulose Nanocrystals (CNC)

Like chitosan, cellulose is also a biopolymer that is abundant in nature, most commonly found in plant matter (15). In an industrial setting, cellulose is extracted from cotton fibers. While native cellulose is environmentally benign and is both hydrophilic and oleophilic, it does not meet the minimum functional properties required for use as an aftermarket carpet treatment (16). The team therefore turned to cellulose derivatives to find a suitable material that can impart hydrophobicity. Cellulose nanocrystals (CNC) were chosen as the most promising and viable alternative due to their widespread use in thin films and coatings in packaging applications (17).

CNC's are known to be elastic, strong, cheaply produced, and can be combined with other materials for added functionality (16). The material would be best applied to carpets as a powder rather than a liquid spray or aerosol to ensure even dispersion and prevent blockages in spray applicators.

Technical Performance

Chitosan shows promising performance as a water barrier, with contact angles of 102° when applied on polyester and 130° when applied on cotton (12). Contact angles over 90° indicate that a material is hydrophobic; the higher the contact angle number, the more hydrophobic the surface (18). In films, cellulose nanocrystals consistently enhance the hydrophobicity of a variety of base materials. A water contact angle of 130.6° was reported for a CNC composite film surface (19). These values indicate moderate performance in terms of hydrophobicity when compared to the performance baseline of Scotchgard™. Oleophobicity for both biopolymers is currently unknown. Chitosan has very high wash resistance, with antimicrobial activity for up to 50 washes in clothing (13). This is even more promising in the context of carpets, which are not washed as often as clothing. Meanwhile, wash resistance data is not known for CNC's.



		Hydrophobicity (Contact Angle)	Oleophobicity	Washability	Source
Bad Actor	PFAS	170°	156°	120+ Washes	Artificial
Biopolymers	Chitosan	102°	DG	50 Washes	Crustacean Exoskeletons
	CNC	>90°	w/PFAS	DG	Cellulose Isolation + Prep
	Key	Best Performance	Medium Performance	Worst Performance	Data Gap (DG)

Figure 1: Technical performance table for chitosan and CNC's.[1]

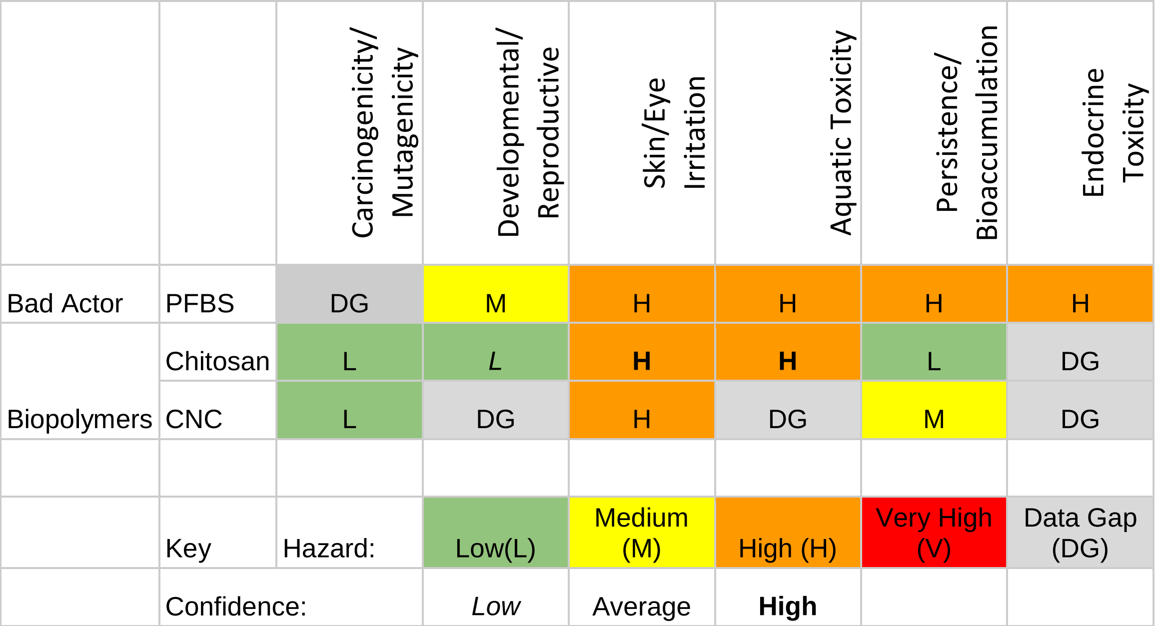
Environmental Health and Safety Performance

Both chitosan and cellulose nanocrystals have significantly improved EH&S performance compared to the PFAS baseline. Chitosan has low carcinogenicity and mutagenicity, and has shown to even exhibit antimutagenic properties by decreasing the effectiveness of mutagens (20). It has also not been found to have developmental toxicity, and has a relatively fast and easy degradation into nontoxic products, a great improvement over the high persistence of PFASs (21). However, chitosan exhibits high skin and eye irritation, indicating that personal protective equipment (PPE) may be necessary for consumers when applying the product (22). The tradeoff for its antimicrobial properties is high aquatic toxicity, which can negatively impact fish at even extremely low concentrations (23). Although there are significant data gaps for EH&S performance of cellulose nanocrystals, there is still evidence that the material is less harmful than PFASs in a number of important categories. While some studies show potential for negative

---

[1] References for EHS and Technical Performance tables can be found in original report, available at: https://bcgc.berkeley.edu/greener-solutions-2020/

health effects such as cytotoxicity and immunosuppression, it is believed that the concentration of CNC's tested was too high for realistic exposure, furthermore there was little evidence to suggest mutagenicity (24). CNC's also earned a moderate hazard score for persistence, with some studies showing a greater potential for persistence after chronic exposure of the lungs, but very efficient bio-degradation compared to PFASs (25). As a tradeoff, CNC's also show high lung irritation (26).



		Carcinogenicity/ Mutagenicity	Developmental/ Reproductive	Skin/Eye Irritation	Aquatic Toxicity	Persistence/ Bioaccumulation	Endocrine Toxicity
Bad Actor	PFBS	DG	M	H	H	H	H
Biopolymers	Chitosan	L	*L*	**H**	**H**	L	DG
	CNC	L	DG	H	DG	M	DG
	Key	Hazard:	Low(L)	Medium (M)	High (H)	Very High (V)	Data Gap (DG)
	Confidence:		*Low*	Average	**High**		

Figure 2: EH&S table for chitosan and CNC's.

Strategy 2: Silicon-Based Materials

Silicon-Dioxide Nanoparticles

Silicon-dioxide nanoparticles are small particles of tunable size between 1-500 nm, which consist of networks of silicon-oxygen bonds. The size of the particles is controlled via the sol-gel process, which combines tetraethylorthosilicate (TEOS) in ethanol with ammonium hydroxide (NH4OH) (27, 28). The ability to tune the particle size is especially important because this determines the level of hydrophobicity and oleophobicity of the coating. They are a class of materials already commonly used in fabric protection products, such as those by Vetro Power and protectME, which feature a simple application method of water-based spray. Silicon-dioxide nanoparticles show a high affinity for attachment to plant and animal fibers such as cotton and silk, due to the abundance of exposed hydroxyl groups. Nylon contains far fewer of these exposed groups, and requires additional treatment with an acid application to retain the silicon-dioxide nanoparticles (29).

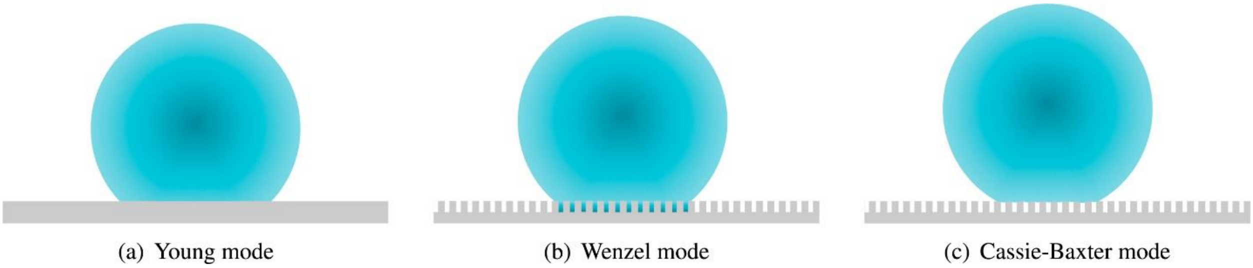


Figure 3: Surface wetting modes affected by surface patterning. Source: Deng, Y. et al. (2018).

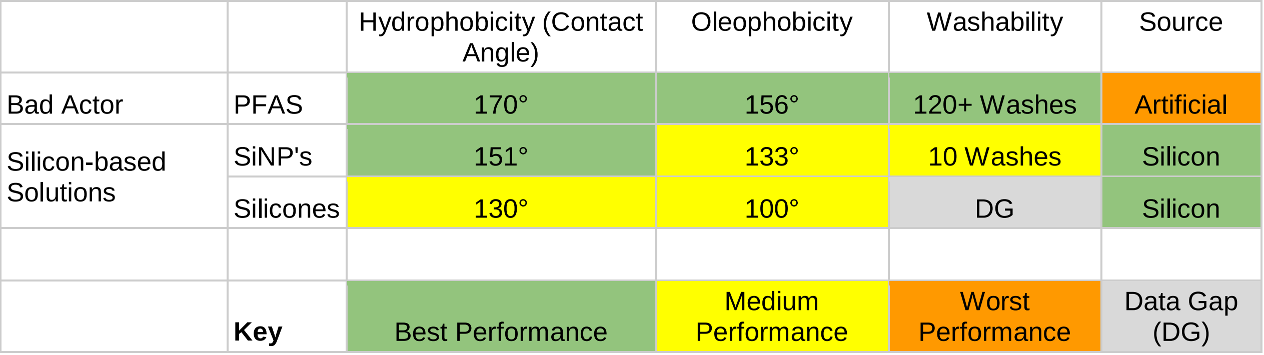
The mechanism of silicon-dioxide nanoparticles' water repellant properties is based on that of the lotus leaf (30). Rather than repelling liquids chemically as in PFASs, or forming a barrier coating as in the biopolymer strategy, this method involves hierarchical rough patterning to create physical liquid repellency. Hierarchical rough patterning involves the formation of micro- and nano-scale structural protrusions at the surface of a material, which trap air and induce Cassie-Baxter wetting, which refers to liquid repulsion via incomplete coating of the surface (Figure 3) (31). Particle size and spacing is especially important in this context because the parameter of "air pocket size" in hierarchical rough patterning determines the relative hydrophobicity and oleophobicity of the surface. Oil has a lower surface tension compared to water, and therefore requires smaller "air pockets" (lower surface energy of the coating) in order to be repelled. Tunability of the particle size has the potential to optimize the surface such that both water and oil can be repelled. Silicon-dioxide nanoparticles also have great potential for functional tunability with inclusion of small molecule additives. For example, hydrophobicity can be enhanced by incorporating molecules capable of chemical liquid repellency, such as sodium stearate (32). Silicon-dioxide nanoparticles can also be functionalized with methyltriethoxysilane (MTES) to achieve oleophobicity alongside hydrophobicity when applied to paper (33).

Silicones and Silanes

Silicones and silanes were researched with a specific emphasis on oleophobicity. While hierarchical rough patterning is effective for achieving water repellency, the surface tension of oil is much lower, due to weaker dipole-dipole interactions as compared to hydrogen bonds in water. An alternate strategy to achieving oleophobicity is increasing the surface energy at the oil/coating interface, which can be achieved with flexibility and molecular dynamics (34, 35). This method of incorporating silicones with nylon fibers has been tested, and has led to impressive results (34). However, the ease of application and feasibility of a safe consumer spray-on formulation remains a challenge. Unlike other alternatives, silicones are not readily soluble in water, potentially resulting in the need for hazardous solvent.

Technical Performance

The primary strength of the silicon-based materials outlined in this section is their compatibility with a wide range of small molecule additives and their resulting functional tunability. Plain, unfunctionalized silicon-dioxide nanoparticles demonstrate only weak hydrophobicity (water contact angle of 100°) and no inherent oleophobicity (36). However, silicon-dioxide nanoparticles functionalized with sodium stearate resulted in a superhydrophobic coating (water contact angle of >150°) when applied to a nylon surface (32). In another example, silicon-dioxide nanoparticles coated with methyltriethoxysilane (MTES) led to both hydro- and oleo-phobic properties, with highly impressive performance: the measured contact angles of oil and water were 149° and 133°, respectively when applied to paper (33). These values correspond to high performance, comparable with PFASs in terms of liquid repellent properties, with moderate washability performance as well (hydrophobicity persisted for over 10 washing cycles) (32). For silicones and silanes, polydimethylsiloxane (PDMS) is the most common silicone, so it is used as a representative compound for this analysis. Overall performance in terms of hydrophobicity and oleophobicity is good for a variety of oils and for water when PDMS is applied to nylon (34). Meanwhile, a functionalized siloxane polymer with alkyl groups of varying lengths also shows moderately favorable performance for both oil and water as well (water contact angle over 90°, improved oil contact angle) (37). Washing performance was not available for silicone and silane materials.



		Hydrophobicity (Contact Angle)	Oleophobicity	Washability	Source
Bad Actor	PFAS	170°	156°	120+ Washes	Artificial
Silicon-based Solutions	SiNP's	151°	133°	10 Washes	Silicon
	Silicones	130°	100°	DG	Silicon
	Key	Best Performance	Medium Performance	Worst Performance	Data Gap (DG)

Figure 4: Technical performance table for silicon-based solutions.

Environmental Health and Safety Performance

Overall, both silicon-dioxide nanoparticles and silicones and silanes are expected to have lower hazards compared to PFASs. However, the small size of silicon-dioxide nanoparticles, and their diverse size range, add complexity to the identification of health hazards, as many benign materials take on toxic effects at the nanoscale (38). However, it should be noted that silicon-dioxide nanoparticles are already widely used in various consumer products, including cosmetics, pharmaceuticals, and food. By themselves, silicon-dioxide nanoparticles were scored as moderately hazardous for mutagenicity and carcinogenicity (38). Although skin and eye irritation were not observed, respiratory irritation and sensitization was observed (39). The class of materials is also known to biodegrade quite quickly, so they are a significant improvement over PFASs in this respect (40). There is, however, evidence of developmental and reproductive toxicity, although this data is limited (38, 41). Tetraethylorthosilicate (TEOS), a major component of silicon-dioxide nanoparticles, was also evaluated for EH&S performance, and was also found to be largely low hazard but with marked hazards for those exposed to its manufacture. The material was found to be moderately skin and eye irritating, but severely irritating to respiratory systems (42).

The two small molecule additives, sodium stearate and MTES were also assessed for hazards of their own. Sodium stearate scored low hazard in carcinogenicity and mutagenicity, and persistence. However, the additive scored high hazard for aquatic toxicity and skin and eye irritation, indicating that care must be taken in the manufacture and disposal of this material. Meanwhile, MTES was found to be exceedingly safe, scoring low hazard in all known categories.[2] This provides an overall picture of silicon-dioxide nanoparticles as a much safer stain repellent material compared to PFASs.

A common challenge of assessing polymers such as PDMS is the lack of EH&S data available for complete polymers, and the changing hazard landscape dependent on the length of the polymer chains in the material. Due to its widespread use, however, more data is available for PDMS. The main concern of using PDMS is its very high aquatic toxicity, high skin/eye irritation potential, and its high persistence, though the material scored low in both carcinogenicity/mutagenicity and developmental/reproductive toxicity. Similarly, a primary component of PDMS, dimethyldichlorosilane, was also evaluated and found to be largely low hazard, with only moderate concern regarding skin/eye irritation. Tetramethoxysilane, a component of the functionalized siloxane polymer, was found to have a very similar hazard profile as dimethyldichlorosilane, with the only difference being high rather than moderate skin/eye irritation. Hazard data for this analysis was sourced from the ECHA substance infocard, The New Zealand EPA's Chemical Classification and Information Database (CCID), and the Danish Advisory List for Self-Classification of Hazardous Substances.

---

[2] Editor's Note: Since the completion of the final report, it was found that MTES had moderate hazard for skin irritation, skin sensitization, and eye irritation.

		Carcinogenicity/ Mutagenicity	Developmental/ Reproductive Toxicity	Skin/Eye Irritation	Aquatic Toxicity	Persistence/ Bioaccumulation	Endocrine Toxicity
Bad Actors	PFBS	DG	M	H	H	H	H
Silicon-Based Solutions	SiNPs	*M*	*H*	_M*_	L	L	L
	TEOS	*L*	DG	*M*	L	L	L
	Sodium Stearate	*L*	DG	H	H	L	DG
	MTES	*L*	*L*	L	L	L	DG
	PDMS	*L*	*L*	H	*V*	H	DG
	Dimethyldichlorosilane	L	L	M	L	L	DG
	Tetramethoxysilane	L	L	H	L	L	DG
	Key	Hazard:	Low(L)	Medium (M)	High (H)	Very High (V)	Data Gap (DG)
		Confidence:	*Low*	Average	**High**		

Figure 5: EH&S performance table for silicon-based solutions.

What was Innovative about the Solution:

The solutions presented by the team were shaped by how the group framed the problem, defined solution criteria, considered sourcing, and identified their final solution recommendation. They first thought beyond the scope of what “carpet protection” typically means. Fluorinated compounds do offer effective textile protection via stain resistance, but in doing so, largely neglect other modes by which carpets can be damaged. PFASs actually overperform for what is needed from a carpet protectant, providing a water contact angle of up to 150° when contact angles of only 90° offer sufficient protection against stains for an average user. While PFASs are ubiquitous as an easy-to-implement water and oil barrier material, they can only perform this single function, and they do so in exchange for serious health hazards. Instead of aiming to outperform PFASs at their strongest function, the team identified alternatives that offer performance levels appropriate for home use while also adding value in categories of protection that PFAS does not perform. For example, rather than overperform at a single function like PFASs do, chitosan is a broadly performing material with lower hydrophobicity than PFASs, but that also confers protection in other relevant ways (antimicrobial, self-healing) (13,14). Matching these additional properties to the needs of a potential consumer, uncovered an opportunity to decrease hazard, and add new value to the product.

The team also considered sustainable sourcing in all of their solutions by proposing to use highly abundant natural sources, including an existing waste stream (chitosan from crustacean shell waste) (10). Using abundant base materials ensures that the products are economically feasible to produce and that potential harm that arises from increased extraction of a new resource is minimized. This is another example of where a product decision can simultaneously improve sustainability as well as lower its cost.

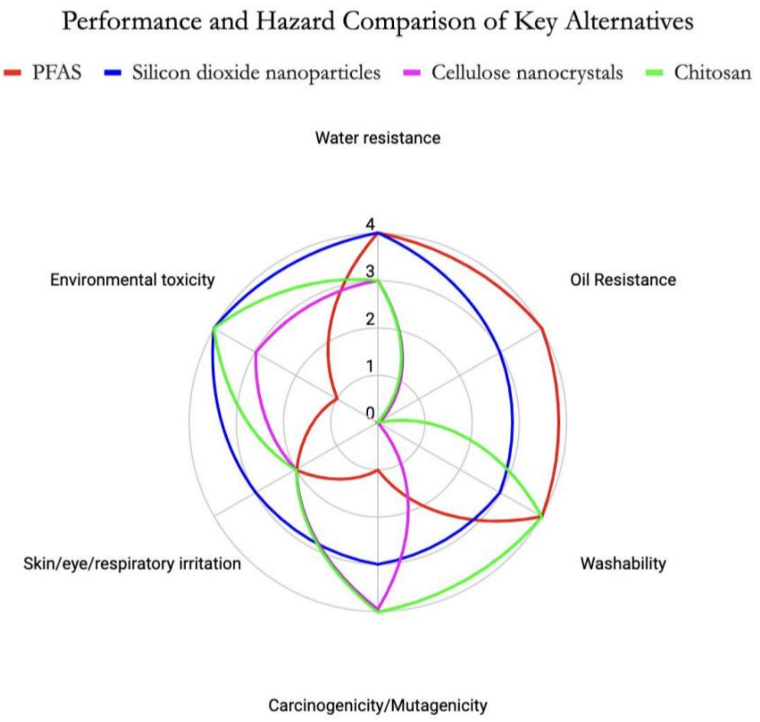


Figure 6: Comparison of PFAS to key alternatives. 4 represents the greatest performance along a technical or safety criterion, 1 is worst, and 0 is a data gap.

The final recommendation by the team is a combination of strategies: chitosan with silicon-dioxide nanoparticles. In Figure 6 above, the relative performance of each solution is compared across six categories: water resistance, oil resistance, washability, carcinogenicity/mutagenicity, skin/eye/respiratory irritation, and environmental toxicity. Pairing chitosan with silicon dioxide nanoparticles covers the largest range of performance categories. Chitosan provides an acceptable baseline of liquid barrier as well as a complete range of carpet protection features. This foundation can then be enhanced with silicon-dioxide nanoparticles, which can provide super hydrophobicity when functionalized with sodium stearate, and oleophobicity when functionalized with MTES (32,33). Both alternatives are soluble in slightly acidic conditions, which suggests compatibility in a combined liquid spray or aerosol formulation. The combination of both materials’ strengths results in a solution that has the potential to offer performance similar to PFASs with additional antimicrobial and self-healing properties.

What was the Impact:

Carpets manufacturers began phasing out certain types of PFASs in 2008. Under pressure from the US EPA, the carpet industry committed to replacing long-chained PFASs with short-chain PFASs, then believed to have lower health risks associated with their use. Research has since shown, however, that short-chain PFASs carry similar health hazards to their long-chained counterparts, and may even permeate the environment more rapidly due to the molecules’ increased mobility through soil and water, and persistent degradation products. Sales of aftermarket treatments for carpets are logically affected by regulations on carpet manufacturing; consumers may be more motivated to purchase aftermarket treatments if pre-treated carpets are not as available, further increasing their exposure to fluorinated compounds.

Additionally, the average lifespan of a carpet ranges from 10 to 20 years, which indicates that PFASs will continue to persist in homes and environments for decades after initial regulation against PFAS products. This makes the need for regulatory action and suitable replacements all the more urgent. The California DTSC named PFASs in the manufacture of carpets and rugs as a priority product effective July 2021, thereby requiring manufacturers to notify consumers of the presence of PFASs in their products. The manufacturers then have the option to submit notice of removing or replacing the chemical of concern/product from production, or report alternative products (2). In parallel, aftermarket treatments containing PFASs for use on converted textiles (including carpets) are listed as a proposed priority product, signaling upcoming regulation controlling their non-essential use (5).

The global fabric protection market, which includes carpet treatments, was valued at USD 1.11 billion in 2018, and is projected to grow at a CAGR of 4.6% from 2019 to 2025 according to a report by Grand View Research. Upholstery protection, which includes fabric protectants applied to carpets, rugs, and sofas, comprised at least 50% of the total market in 2018 (43), which translates into approximately USD 555 million. While PFASs are present in these products at low concentrations, replacing PFASs within such a large industry could result in the avoided use of hundreds of thousands pounds (approximately 750,000 pounds) each year.

Aftermarket treatments are a particularly important target for reformulation when considering improved EH&S performance of the product. As a consumer-applied product, consumers are even more exposed to PFAS materials than in carpet coatings added at the manufacturing phase. Consumers are at risk of inhaling aerosols during the application process, and untrained users of the product might not wear PPE even if it is recommended. After application, carpets are a surface that is touched often with bare skin and regular wear and tear of the carpet by walking may also release coated fibers into the air. Hand-to-mouth behavior of small children also introduces an oral exposure route (44). These many routes of repeated exposure to the carpet protectant materials necessitate alternatives that significantly reduce the health hazards posed by PFAS products.

References:

1. *History of PFAS and 3M*. https://www.3m.com/3M/en_US/pfas-stewardship-us/pfas-history/.
2. *Effective July 1, 2021: Carpets and Rugs with Perfluoroalkyl or Polyfluoroalkyl Substances (PFASs)*. https://dtsc.ca.gov/scp/carpets-and-rugs-with-perfluoroalkyl-and-polyfluoroalkyl-substances-pfass/.
3. Vallette, J.; Stamm, R.; Lent, T.; *Eliminating Toxics in Carpet: Lessons for the Future of Recycling*; Healthy Building Network, 2017. https://s3.amazonaws.com/hbnweb.prod/uploads/files/eliminating-toxics-in-carpet-lessons-for-the-future-of-recycling.pdf
4. Renner, R. The Long and the Short of Perfluorinated Replacements. *Environmental Science and Technology*. January 1, 2006, pp 12–13. https://doi.org/10.1021/es062612a.
5. *Proposed Priority Product: Treatments Containing Perfluoroalkyl or Polyfluoroalkyl Substances for Use on Converted Textiles or Leathers*. https://dtsc.ca.gov/scp/treatments-with-pfass/.
6. Bălan, S. A.; Mathrani, V. C.; Guo, D. F.; Algazi, A. M. Regulating Pfas as a Chemical Class under the California Safer Consumer Products Program. *Environmental Health Perspectives*. Public Health Services, US Dept of Health and Human Services 2021, pp 1–9. https://doi.org/10.1289/EHP7431.
7. *Basic Information on PFAS*. https://www.epa.gov/pfas/basic-information-pfas.
8. *Paraffin application in industry*. https://atdmco.com/wiki-paraffin+application+in+industry-136.html.
9. Rajeswari, A.; Gopi, S.; Jackcina Stobel Christy, E.; Jayaraj, K.; Pius, A. Current Research on the Blends of Chitosan as New Biomaterials. In *Handbook of Chitin and Chitosan*; Elsevier, 2020; pp 247–283. https://doi.org/10.1016/b978-0-12-817970-3.00009-2.
10. Prabaharan, M. Sources of Chitosan. In *Chitosan and Its Derivatives as Promising Drug Delivery Carriers*; ASME Press, 2013; pp 3–3. https://doi.org/10.1115/1.860052_ch2.
11. *Supplier of Chitosan Antimicrobial Textile Treatments*. https://tidalvisionusa.com/textiles/.
12. Roy, J.; Salaün, F.; Giraud, S.; Ferri, A.; Guan, J. Chitosan-Based Sustainable Textile Technology: Process, Mechanism, Innovation, and Safety. In *Biological Activities and Application of Marine Polysaccharides*; InTech, 2017. https://doi.org/10.5772/65259.
13. Ye, W.; Xin, J. H.; Li, P.; Lee, K. L. D.; Kwong, T. L. Durable Antibacterial Finish on Cotton Fabric by Using Chitosan-Based Polymeric Core-Shell Particles. *J. Appl. Polym. Sci.* 2006, *102* (2), 1787–1793. https://doi.org/10.1002/app.24463.
14. Yılmaz Atay, H.; Eral Doğan, L.; Çelik, E. Investigations of Self-Healing Property of Chitosan-Reinforced Epoxy Dye Composite Coatings. *J. Mater.* 2013, *2013*, 1–7. https://doi.org/10.1155/2013/613717.
15. Lavanya, D.; Kulkarni, P.; Dixit, M.; Kanth Raavi, P.; Naga Vamsi Krishna, L. Sources of Cellulose and Their Applications—A Review. *IJDFR* 2011, *2* (6), 1–20.
16. Shankaran, D. R. Cellulose Nanocrystals for Health Care Applications. In *Applications of Nanomaterials*; Elsevier, 2018; pp 415–459. https://doi.org/10.1016/b978-0-08-101971-9.00015-6.
17. Hubbe, M. A.; Ferrer, A.; Tyagi, P.; Yin, Y.; Salas, C.; Pal, L.; Rojas, O. J. Nanocellulose in Thin Films, Coatings, and Plies for Packaging Applications: A Review. *BioRes* 2017, *12* (1), 2143–2233.
18. Hebbar, R. S.; Isloor, A. M.; Ismail, A. F. Contact Angle Measurements. In *Membrane Characterization*; Elsevier Inc., 2017; pp 219–255. https://doi.org/10.1016/B978-0-444-63776-5.00012-7.
19. Sudhakar, Y. N.; Selvakumar, M.; Bhat, D. K. Methods of Preparation of Biopolymer Electrolytes. In *Biopolymer Electrolytes*; Elsevier, 2018; pp 35–52. https://doi.org/10.1016/b978-0-12-813447-4.00002-9.

20. Chang, S. H.; Wu, C. H.; Tsai, G. J. Effects of Chitosan Molecular Weight on Its Antioxidant and Antimutagenic Properties. *Carbohydr. Polym.* 2018, *181*, 1026–1032. https://doi.org/10.1016/j.carbpol.2017.11.047.
21. Kean, T.; Thanou, M. Biodegradation, Biodistribution and Toxicity of Chitosan. *Advanced Drug Delivery Reviews*. Elsevier January 31, 2010, pp 3–11. https://doi.org/10.1016/j.addr.2009.09.004.
22. *Chitosan*. https://echa.europa.eu/substance-information/-/substanceinfo/100.122.259.
23. Bullock, G.; Blazer, V.; Tsukuda, S.; Summerfelt, S. Toxicity of Acidified Chitosan for Cultured Rainbow Trout (Oncorhynchus Mykiss). *Aquaculture* 2000, *185* (3–4), 273–280. https://doi.org/10.1016/S0044-8486(99)00359-2.
24. Kurakula, M.; N., N. R. Prospection of Recent Chitosan Biomedical Trends: Evidence from Patent Analysis (2009–2020). *International Journal of Biological Macromolecules*. Elsevier B.V. December 15, 2020, pp 1924–1938. https://doi.org/10.1016/j.ijbiomac.2020.10.043.
25. Halib, N.; Ahmad, I. Nanocellulose: Insight into Health and Medical Applications. In *Handbook of Ecomaterials*; Springer International Publishing, 2018; pp 1–19. https://doi.org/10.1007/978-3-319-48281-1_5-1.
26. Stoudmann, N.; Schmutz, M.; Hirsch, C.; Nowack, B.; Som, C. Human Hazard Potential of Nanocellulose: Quantitative Insights from the Literature. *Nanotoxicology*. Taylor and Francis Ltd. October 20, 2020, pp 1241–1257. https://doi.org/10.1080/17435390.2020.1814440.
27. Bae, G. Y.; Min, B. G.; Jeong, Y. G.; Lee, S. C.; Jang, J. H.; Koo, G. H. Superhydrophobicity of Cotton Fabrics Treated with Silica Nanoparticles and Water-Repellent Agent. *J. Colloid Interface Sci.* 2009, *337* (1), 170–175. https://doi.org/10.1016/j.jcis.2009.04.066.
28. Schmidt, H.; Jonschker, G.; Goedicke, S.; Mennig, M. The Sol-Gel Process as a Basic Technology for Nanoparticle-Dispersed Inorganic-Organic Composites. *J. Sol-Gel Sci. Technol.* 2000, *19* (1–3), 39–51. https://doi.org/10.1023/A:1008706003996.
29. Li, F.; Xing, Y.; Ding, X. Silica Xerogel Coating on the Surface of Natural and Synthetic Fabrics. *Surf. Coatings Technol.* 2008, *202* (19), 4721–4727. https://doi.org/10.1016/j.surfcoat.2008.04.048.
30. Ensikat, H. J.; Ditsche-Kuru, P.; Neinhuis, C.; Barthlott, W. Superhydrophobicity in Perfection: The Outstanding Properties of the Lotus Leaf. *Beilstein J. Nanotechnol.* 2011, *2* (1), 152–161. https://doi.org/10.3762/bjnano.2.19.
31. Deng, Y.; Mager, D.; Bai, Y.; Zhou, T.; Liu, Z.; Wen, L.; Wu, Y.; Korvink, J. G. Inversely Designed Micro-Textures for Robust Cassie–Baxter Mode of Super-Hydrophobicity. *Comput. Methods Appl. Mech. Eng.* 2018, *341*, 113–132. https://doi.org/10.1016/j.cma.2018.06.034.
32. Teli, M. D.; Annaldewar, B. N. Superhydrophobic and Ultraviolet Protective Nylon Fabrics by Modified Nano Silica Coating. *J. Text. Inst.* 2017, *108* (3), 460–466. https://doi.org/10.1080/00405000.2016.1171028.
33. Sheen, Y. C.; Chang, W. H.; Chen, W. C.; Chang, Y. H.; Huang, Y. C.; Chang, F. C. Non-Fluorinated Superamphiphobic Surfaces through Sol-Gel Processing of Methyltriethoxysilane and Tetraethoxysilane. *Mater. Chem. Phys.* 2009, *114* (1), 63–68. https://doi.org/10.1016/j.matchemphys.2008.07.132.
34. Shabanian, S.; Khatir, B.; Nisar, A.; Golovin, K. Rational Design of Perfluorocarbon-Free Oleophobic Textiles. *Nat. Sustain.* 2020, *3* (12), 1059–1066. https://doi.org/10.1038/s41893-020-0591-9.
35. Cheng, D. F.; Urata, C.; Yagihashi, M.; Hozumi, A. A Statically Oleophilic but Dynamically Oleophobic Smooth Nonperfluorinated Surface. *Angew. Chemie* 2012, *124* (12), 3010–3013. https://doi.org/10.1002/ange.201108800.
36. Petcu, C.; Purcar, V.; Spătaru, C. I.; Alexandrescu, E.; Şomoghi, R.; Trică, B.; Niţu, S. G.; Panaitescu, D. M.; Donescu, D.; Jecu, M. L. The Influence of New Hydrophobic Silica Nanoparticles on the Surface Properties of the Films Obtained from Bilayer Hybrids. *Nanomaterials* 2017, *7* (2). https://doi.org/10.3390/nano7020047.

37. Urata, C.; Masheder, B.; Cheng, D. F.; Hozumi, A. How to Reduce Resistance to Movement of Alkane Liquid Drops across Tilted Surfaces without Relying on Surface Roughening and Perfluorination. *Langmuir* 2012, *28* (51), 17681–17689. https://doi.org/10.1021/la303829p.
38. Murugadoss, S.; Lison, D.; Godderis, L.; Van Den Brule, S.; Mast, J.; Brassinne, F.; Sebaihi, N.; Hoet, P. H. Toxicology of Silica Nanoparticles: An Update. *Archives of Toxicology*. Springer Verlag September 1, 2017, pp 2967–3010. https://doi.org/10.1007/s00204-017-1993-y.
39. Han, H.; Park, Y. H.; Park, H. J.; Lee, K.; Um, K.; Park, J. W.; Lee, J. H. Toxic and Adjuvant Effects of Silica Nanoparticles on Ovalbumin-Induced Allergic Airway Inflammation in Mice. *Respir. Res.* 2016, *17* (1). https://doi.org/10.1186/s12931-016-0376-x.
40. Michel, K.; Scheel, J.; Karsten, S.; Stelter, N.; Wind, T. Risk Assessment of Amorphous Silicon Dioxide Nanoparticles in a Glass Cleaner Formulation. *Nanotoxicology* 2013, *7* (5), 974–988. https://doi.org/10.3109/17435390.2012.689881.
41. Hu, H.; Fan, X.; Guo, Q.; Wei, X.; Yang, D.; Zhang, B.; Liu, J.; Wu, Q.; Oh, Y.; Feng, Y.; Chen, K.; Hou, L.; Gu, N. Silicon Dioxide Nanoparticles Induce Insulin Resistance through Endoplasmic Reticulum Stress and Generation of Reactive Oxygen Species. *Part. Fibre Toxicol.* 2019, *16* (1). https://doi.org/10.1186/s12989-019-0327-z.
42. *Tetraethyl Orthosilicate*. https://pubchem.ncbi.nlm.nih.gov/compound/Tetraethyl-orthosilicate.
43. *Fabric Protection Market Size, Share & Trends Analysis Report By Application (Apparel, Footwear, Upholstery), By Region (North America, Asia Pacific, MEA), And Segment Forecasts, 2019 - 2025*. https://www.grandviewresearch.com/industry-analysis/fabric-protection-market.
44. Ter Burg, W.; Bremmer, H. J.; Van Engelen, J. G. M. *Oral Exposure of Children to Chemicals via Hand-to-Mouth Contact*. RIVM 320005004/2007; Centre for Substances and Integrated Risk Assessment, 2008. https://www.rivm.nl/publicaties/oral-exposure-of-children-to-chemicals-via-hand-to-mouth-contact.