

# **Finding Safer Alternatives to the PFAS-free Moisture Barrier in Structural Firefighting Gear**

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## **Executive Summary**

The International Association of Firefighters (IAFF) tasked us with proposing safer alternative materials that meet the required functions of the PTFE moisture barrier in firefighter turnout gear. The composition of firefighter turnout gear has come under scrutiny due to the carcinogenic health effects of the chemicals found in the gear. Firefighter turnout gear is generally composed of three layers: an inner thermal layer, a middle moisture barrier, and an outer shell. The moisture barrier layer is of particular concern due to the incorporation of poly- and perfluoroalkyl substances (PFAS). PFAS are a group of “forever chemicals” aptly named due to their persistence and slow degradation in the environment. A common PFAS used in the moisture barrier is polytetrafluoroethylene (PTFE). PTFE is a synthetic fluoropolymer (a polymer with multiple fluorine carbon bonds) that is effective as a moisture barrier because it is water and oil resistant, thermally stable, and breathable (Graham et al, 2020).

After conducting hazard and technical performance assessments on a variety of PFAS-free materials, we propose applying a hydrophobic coating or laminating a hydrophobic material onto a fiber to achieve a PFAS-free moisture barrier that minimizes hazards while meeting the required functions – water and oil resistant, thermally stable, and breathable. Combining a fiber with a coating and a laminate all together could enhance moisture barrier properties further, but more research is needed to make a declarative statement on the effectiveness. We also propose changes to the National Fire Protection Association (NFPA) turnout gear testing standards, which would allow for PFAS-free materials to be more practically considered.

## **Introduction**

### *Challenge*

Our partners’ challenge was to identify safer alternatives to the PTFE laminate moisture barrier currently approved by the National Fire Protection Association (NFPA) 1971 Standards, which certify firefighter turnout gear. We were partnered with the International Association of Firefighters (IAFF), a labor union made up of firefighters and scientists, representing firefighters and paramedics in the United States and Canada.

### *Background*

The composition of firefighter turnout gear has come under scrutiny due to the adverse health effects of per- and polyfluoroalkyl Substances (PFAS) found in the gear. A class of over 9,000 unique, well-studied PFAS chemicals has been linked to certain cancers, thyroid disease, reproductive problems, and other serious adverse health effects (Goodrich et al). Firefighters are already exposed to many carcinogenic air pollutants from smoke, and firefighting materials, such as foams – their uniforms should not be an additional occupational health concern.

Existing firefighter turnout gear is made up of three layers: an inner thermal layer closest to the skin, a middle moisture barrier, and a durable water repellent (DWR) outer shell. The primary function of the moisture barrier is to block penetration by water, water vapor, liquid chemicals, and heat, while allowing perspiration and body heat to escape (Graham et al, 2020). Liquid resistance and vapor permeability is particularly important for the prevention of steam burns which occur if water and heat get trapped inside the gear (Su et al., 2018; “Why Firefighters Get Steam Burns,” 2015).

The NFPA sets standards on Protective Ensembles for Structural Fire Fighting and Proximity Fire Fighting in the United States and Canada. The current moisture barrier layer, approved by the NFPA 1971 Standards, contains a polytetrafluorethylene (PTFE) laminate layer. PTFE, a synthetic fluoropolymer, is one of the most well-known and applied PFAS. It is effective in turnout gear due to its water and oil resistance, thermal stability, and breathability (Graham et al, 2020). PTFE itself is considered inert; however, other PFAS chemicals used in the manufacturing process are present on the gear and pose health risks to the wearer as well as persist in the environment. Studies found that PFAS migrate across turnout gear layers into untreated material such as the inner thermal layer. Elevated blood levels of PFAS have been measured in firefighters, and dermal absorption from direct skin contact with turnout gear is one key exposure route (Graham et al, 2020, Trowbridge et al., 2020, Laitinen et al., 2014).

Firefighting as an occupational exposure is classified as a Class 1 carcinogen (Demers et al., 2022). The National Institute for Occupational Safety and Health (NIOSH) reports that firefighters have a 9% higher risk of cancer diagnosis and a 14% higher risk of cancer-caused mortality than the total U.S. population (Daniels et. al., 2013). It is also important to consider the healthy worker effect in this context. The healthy worker effect suggests that workers are typically healthier than the general population due to their ability to work, further emphasizing the significance of these statistics.

Each turnout gear ensemble has a lifespan of ten years or fewer depending on condition, as required by NFPA 1971 (National Fire Protection Association). Aptly named “forever chemicals,” PFAS are extremely bioaccumulative and persistent in the environment, so promptly finding safer alternatives to gear that could be worn for up to a decade is important for preventing adverse health outcomes for firefighters and future degradation to the environment.

## **Approach**

Over the past four months, our team has researched the political landscape of firefighter turnout gear testing standards, the makeup of a moisture barrier and its required functions, and conducted human health and environmental hazard and technical performance assessments on potential

alternative materials. Although our challenge is multifaceted and could be evaluated from the manufacturing-side, consumer-side, or throughout the entire life cycle, we chose to address the consumer (firefighter) issue of PFAS in firefighter turnout gear through a two-pronged policy and science approach.

*Policy Approach*

In considering alternatives to the PTFE laminate moisture barrier, we conducted a review of the NFPA 1971 performance standards used to evaluate firefighter turnout gear in relation to the European Union (EN 469) and Australian (AUS) standards. From our partners guidance, we chose these standards as a comparison, given their overall similarity to NFPA 1971. The NFPA is a self-funded non-governmental agency, led largely by industry stakeholders, with no official regulatory authority (About NFPA, n.d.). In our first partner meeting, they expressed concern that current gear may be over-engineered due to over-prescriptive standards that go beyond what is required for safe and functional turnout gear, thus limiting functional PFAS-free alternatives.

Table 1 presents a comparison of the NFPA 1971 Standards used in North America to the EN 469 and AUS standards. We used this table to assess differences in the standards and determine instances of over-prescriptiveness leading to overengineered turnout gear.

**Table 1**

Requirements	NFPA	EN 469 - Level 2 (Structural) European Union	AUS (Australia)
<b>Heat/Thermal Resistance</b>	Shall not shrink > <b>10%</b> in any direction.	At 5-minute exposure 180°C: Shall not shrink > <b>5%</b> in any direction. No ignition. No melting.	<b>X</b>
<b>Water penetration (resistance)</b>	Minimum water penetration resistance of <b>172 kPa (25 psi)</b> .	Minimum water resistance of <b>20 kPa</b>	Using the rate of water pressure increase of 9.8 mbar/min and water temperature of 20 °C shall achieve ≥ 200 cm of H2O
<b>Tear resistance</b>	Tear strength of not less than <b>22 N (5 lbf)</b> .	Tear strength of no less than <b>30 N</b>	Coated materials shall give a tear strength equal to or greater than <b>25 N</b>
<b>Flame Resistance</b>	Char length < <b>100 mm</b> . Afterflame < <b>2 seconds</b> .	<b>X</b>	<b>X</b>
<b>Cleaning Shrinkage Resistance</b>	Cannot shrink more than <b>5%</b>	Shall not shrink more than <b>3 %</b> (woven) Shall not shrink more than <b>5%</b> (non-woven)	At a temperature of (260 0 +5 ) °C, no material shall melt, drip, ignite or shrink more than <b>5 %</b>

<b>Liquid Chemical Resistance</b>	No liquid can penetrate any sample for <b>1 hour</b>	No penetration to innermost surface, index of repellency > <b>80%</b>	Clothing shall give > <b>80 %</b> run off with no penetration to the innermost surface
<b>Viral Penetration Resistance</b>	Shall allow no penetration of the Phi-X-174 bacteriophage for at least 1 hour.	<b>X</b>	<b>X</b>
<b>Light Degradation Resistance</b>	Water shall not appear on the surface of the specimen. *Garment is exposed to harsh light for 40 hours	<b>X</b>	<b>X</b>
<b>Water Vapor Resistance</b>	<b>X</b>	Must be less than or equal to <b>30 m<sup>2</sup>Pa/W</b>	After pre-treatment in accordance with Clause 4.1.3, the complete component assembly shall achieve a water vapour resistance of less than 20.0 m <sup>2</sup> ·Pa/W

The light degradation (also known as the “UV light test”) and viral penetration tests are included in the NFPA standards, but excluded from the European and Australian standards. The moisture barrier sits inside the other two turnout gear layers and does not come into contact with UV light, making the UV light test unnecessary. A PTFE laminate is the only material that meets this test, so removing the UV test would allow for PFAS-free moisture barrier options. In May 2021, a Tentative Interim Amendment (TIA) was filed by the IAFF to remove the UV test from the standards, but the NFPA denied it and subsequent appeals by the IAFF. In their appeal the IAFF stated, “The UV light degradation test for moisture barriers is illogical, not supported by science, and stands as a hurdle to advancing the state of the art in firefighter PPE” (Latest, n.d.). One retired battalion chief of the New Haven CT Fire Department said, “Firefighters should be fighting fires, not NFPA and the gear companies” (Latest, n.d.).

The viral penetration test is intended to test the fabric for resistance to liquid or bloodborne pathogens. This test is also unnecessary for the middle layer moisture barrier to meet. Firefighters regularly wear their whole ensemble, whether they are responding to a fire or paramedic services and the DWR outer shell blocks viral particles from interacting with the moisture barrier.

Presently, a first draft of NFPA 1970 is out and open for public comment until January 4th, 2023. NFPA 1970 falls under a custom review cycle due to the Emergency Response and Responder Safety Document Consolidation Plan. The consolidation plan for 1970 entails combining NFPA 1971, NFPA 1975, NFPA 1981, and NFPA 1982. In the NFPA 1970 draft, the light degradation test is not mentioned anywhere since firefighters have been advocating for its removal. However, there is not any movement currently to reconsider the viral penetration test. Following public comment on the first draft, the NFPA anticipates that the Second Draft Reports will be posted for

public review in the Fall of 2023 (NFPA, 2022).

In conclusion, two NFPA 1971 tests – light degradation and viral resistance – are unnecessary for the moisture barrier to meet and are prohibiting PFAS-free options from coming to market. The remaining and relevant standards will be used as technical performance requirements for our alternatives assessment, along with the addition of water vapor transmission, water vapor resistance, and pore size tests, which are not included in the NFPA 1971 standards, but reasonable for a moisture barrier to meet.

### *Science Approach*



**Figure 1** By examining components of the current expanded PTFE (ePTFE) moisture barrier, we started to identify possible alternatives. For example, GORE® PARALLON™ Liner System is a commercially available moisture barrier in firefighter turnout gear made by Gore-tex composed of three layers (exterior layer, middle layer, and body-side layer) that each contain a ePTFE film laminate (Image 1). The exterior layer contains Nomex, a flame resistant fabric, and is laminated with an ePTFE film; the middle layer is made of a KEVLAR/NOMEX blend and laminated with an ePTFE film; the body-side layer is made of a KEVLAR, NOMEX, LENZING fiber blend and laminated with an ePTFE film. Based on this model moisture barrier, the alternatives were broken into three categories: fibers, coatings, and laminates (GORE® PARALLON™ Liner System, 2022).

### **Technical Performance**

The alternatives were compared to the following NFPA 1971 requirements: Heat/Thermal Resistance, Water Penetration (resistance), Liquid Chemical Resistance, and Tear Resistance. Direct comparisons of literature values to the NFPA standard values were made for the tear resistance and water penetration resistance, however, proxies were required for the other standards due to a lack of similar testing in the literature. For example, the Heat/Thermal (resistance) NFPA requirement is that the moisture barrier shall not shrink more than 10% in any direction. The proxy for the Heat/Thermal (resistance) requirement was thermal resistance – the measure of the temperature difference by which a material resists heat flow. Similarly, a proxy was required for the liquid chemical resistance test. The liquid chemical resistance requirement is that no liquid tested (aqueous film-forming foam, 37% by weight sulfuric acid solution, fire-resistant hydraulic fluid, surrogate gasoline fuel, chlorinated solution) penetrate the moisture barrier for 1 hour. The proxy to the liquid chemical resistance requirement is the water contact angle. Water contact angle is the measure of angle a drop of liquid makes with a solid. A water contact angle greater than 90° means the surface is hydrophobic and



a water contact angle less than 90° means the surface is hydrophilic (Law, 2014). A higher water contact angle will prevent the wetting of the material.

We also analyzed additional performance metrics to evaluate how breathable and comfortable alternative materials can be. Additional performance metrics to evaluate the breathability and comfortability of the material were analyzed. Since firefighters work in very hot settings, their gear needs to be breathable so they don't overheat. These additional performance metrics were pore size, water vapor transmission, and water vapor resistance. One purpose of the moisture barrier is to prevent steam burns from sweat or water that becomes trapped between the turnout gear and the skin. By optimizing the pore size so water vapor can pass through the pores, but liquid water cannot, the breathability of the material can be increased and steam burns can be prevented. Water vapor transmission rate is a measure of the rate at which water vapor passes through a fiber or membrane at a certain humidity. The higher the water vapor transmission rate, the higher the breathability of the material. For example, dry-fit clothing and active-wear have a high water vapor transmission rate. The third additional performance metric, water vapor resistance, is a requirement in the EN (European) Protective clothing for firefighters standards. Water vapor resistance is the material's reluctance to allow water vapor to pass through (Insulation Basics, 2019). The lower the water vapor resistance, the higher the breathability.

Due to lack of values matching the NFPA standards, the flame retardant coatings were evaluated based on different performance metrics found in literature. Due to a lack of data for the flame retardant coatings, different performance metrics found in the literature were evaluated and were not evaluated for the laminates and fibers. The two other performance metrics are thermal decomposition (5%), defined in the paper as the temperature at which 5% by weight of the material decomposed, and char length (Lin, 2019). The char length measured in the papers is different from the NFPA standard because the fiber was exposed to flames for a longer period of time than materials are exposed to in the NFPA standards.

Rankings for technical standards are either: the material meets the standard (**yes** or **no**) found in Table 2, or the material is ranked on a scale (**optimal**, **sub-optimal**, or **poor**) found in Table 3. The scales were determined based on the current materials used in the moisture barrier as well as information provided in the literature. **Data gaps** are marked DG and represent values not found in the literature.

**Table 2: Ranking system for whether or not a material meets the technical standard**

Metric	Meets Standard	Does Not Meet Standard
Water Vapor Resistance	>172 kPa (25 Pa)	< kPa (25 Pa)
Heat/Thermal Resistance	>0.008 m <sup>2</sup> K/W	<0.008 m <sup>2</sup> K/W
Tear Resistance	>22 N	<22N
Water Vapor Resistance (EU standard)	<30 m <sup>2</sup> Pa/W	>30 m <sup>2</sup> Pa/W

**Table 3: Ranking system for the ability of a material to meet the technical standard**

Metric	Optimal	Sub-optimal	Poor
Liquid Chemical Resistance (Water Contact Angle)	>100°	70°-100°	0-69°
Pore Size (diameter, μm)	>0.004 and <1	1-100	>100
Water Vapor Transmission (g/(m <sup>2</sup> day))	>1500	750-1500	<750
Thermal Decomposition (5%) Temperature (°C)	>300	150-300	<150
Char Length	<2mm	2mm-1cm	>1cm

### Hazard Assessment

We evaluated the environmental and health hazards associated with our alternatives of interest in order to determine their viability from a risk perspective. We also conducted a hazard assessment of the chemicals both used in and to produce the current moisture barrier and a regrettable substitution brominated flame retardant that served as an alternative to PFAS – otherwise known as “bad actor” chemicals that we are trying to find alternatives for. In our assessments, we are prioritizing reducing hazards associated with Group I Human Health Endpoints like carcinogenicity. While we are aware of concerns of risks posed to manufacturers, our scope focuses on major risks to our firefighting population.

Hazard rankings were categorically assigned (**Very High**, **High**, **Medium**, **Low**, and **Very Low**) for each chemical of interest for specific endpoints. We used a stepwise

process to assign these rankings. First, we looked at hazard assignments from the GreenScreen Guidance Document for Hazard Assessment (an open source hazard ranking system used by researchers, product formulators, and certifiers). Then we used European Chemical Agency (ECHA) dossiers on chemicals registered in the European Union (EU) through REACH (an EU regulation that requires hazard information on chemicals manufactured in or imported to the EU). If there were still data gaps, we conducted a literature search on the hazards associated with the chemical of interest.

We assigned confidence rankings associated with these hazards, which were visualized by shading (a darker shade indicating higher confidence and a lighter shade indicating lower confidence). High confidences were assigned to hazard rankings clearly ranked in GreenScreen. Medium confidences were assigned to hazard rankings that were extrapolated from a range in GreenScreen (e.g. given a range of **Very High-Medium**, we chose a **High** hazard), based on modeled or unverified values, or extrapolated from different GreenScreen ranking entities. Low confidences were assigned to hazard rankings determined by toxicity values (e.g. No Observed Adverse Effect Levels/NOAELs or Lethal Dose/LD50s) provided by ECHA or a literature search that were then compared to known values from high hazard chemicals or ECHA designated low hazard rankings determined from preliminary animal studies.

Once these hazard assessments were conducted, we compared the results among the bad actor chemicals and potential alternatives, to determine whether the alternatives minimized hazards relative to the bad actors. We also assessed the hazards related to our potential alternatives independent of our bad actor chemicals in order to determine whether our alternatives are viable on a scale of absolute risk.

### **“Bad Actor” Chemicals Hazard Assessment**

We initially conducted a hazard assessment on relevant PFAS chemicals used in PTFE polymerization and a brominated flame retardant that is a known regrettable substitution for PFAS-based flame retardants. Specifically, we looked at the following: PTFE; Tetrafluoroethylene (TFE) - the monomer used to produce PTFE; Perfluorooctanoic acid (PFOA) and Perfluorooctanesulfonic acid (PFOS) - two legacy/“C8” PFAS used as surfactants in the production of PTFE; Hexafluoropropylene oxide dimer acid (known as GenX) and Perfluorodecanoic acid (PFDA) - two novel/“C6” PFAS used as replacement for the legacy PFAS; and Tetrabromobisphenol A (TBBPA) - a brominated flame retardant used in textiles that is a known regrettable substitution of PFAS.

All our bad actor chemicals are extremely persistent in the environment and PFOA, PFOS, and GenX are known to bioaccumulate in the human body. TFE, PFOA, PFOS, and TBBPA are known carcinogens (Prop 65). All monomers associated with PTFE

synthesis and the brominated flame retardant TBBPA cause damage to offspring during pregnancy and are considered developmentally toxic. PFOA, PFOS, PFDA, and TBBPA are considered potential endocrine disruptors, and TFE and PFOA are considered neurotoxic.

Across the board, each monomer used to synthesize PTFE poses a high hazard related to at least one Group I Human Health Endpoint (carcinogenicity, reproductive/developmental toxicity, and endocrine activity). The well-studied PFAS - PFOA and PFOS - pose a high hazard to all Group I and II Human Health Endpoints, indicating that other understudied PFAS like GenX and other “alternatives” to these legacy PFAS could pose similar health risks. The brominated flame retardant TBBPA poses a high hazard to all Group I Human Health Endpoints, indicating that other halogenated chemicals could pose a similar risk and should not be considered as alternatives.

While PTFE is considered inert with minimal hazards, the surfactants and monomers used to produce PTFE are evidently toxic. Surfactants not properly removed after PTFE synthesis are of particular concern due to their presence throughout firefighter turnout gear

## **Strategies**

### *Strategy 1: Fibers*

The base of the moisture barrier is the fiber. Since this is the base layer, even if fibers do not meet all of the standards, it is reasonable they could be modified by other materials to enhance their moisture barrier properties.

### **Technical Performance**

#### **Cellulose Based Fibers**

*Cellulose* is a polysaccharide consisting of a linear chain of D-glucose molecules. Cellulose is a primary component of the cell wall and is secreted by some bacteria to form biofilms. In general, fibers are produced by dissolving natural materials like wood pulp and regenerating them via extrusion and precipitation (Felgueiras, 2021). Examples of cotton based fibers include linen and cotton. These fibers are absorbent, breathable, non-toxic, and biodegradable, however, they are highly combustible; for this reason, modifications to the fibers may be necessary for them to act as sufficient moisture barriers in firefighter turnout gear. In addition, cellulose can also be spun into cellulose nanofibers that are lightweight and have higher barrier properties related to certain gasses when compared to other cellulose fibers (Cellulose Nanofiber Manufacturing, n.d.).

*Cotton* had a low water contact angle, but had a high water vapor transmission rate and low water vapor resistance. Additionally, cotton met the tear resistance requirements. Although cotton is a breathable fabric that is comfortable for firefighters to wear, modification of cotton is necessary to increase the water contact angle and the thermal resistance of the material (Appendix V and VI).

*Cellulose nanofibers* had many data gaps in the thermal resistance, water penetration resistance, and tear resistance standards. Although the pore size was optimal, the water contact angle was below 90°, meaning the material is hydrophilic. This is not ideal for the moisture barrier since the fiber is likely to absorb water; however, this can be modified with some modifications (Appendix V and VI).

*Lyocell*, also marketed as Tencel, is a semisynthetic fabric made from regenerated cellulose. It has similar properties to cotton and linen; however, it is reported to have a greater breathability and be 50% more absorbent than cotton. It is a “greener” fabric compared to cotton and other cellulose based fabrics due to safer chemicals used in the manufacturing process (Chambers, 2022). Lyocell performed well in the breathability performance metrics including pore size, water vapor transmission rate, and water vapor resistance. There were data gaps for the thermal resistance and water contact angle. Measures must be taken to decrease the flammability of the fiber and increase the liquid chemical resistance. (Appendix V, VI, and X)

*Viscose Rayon* is a semisynthetic fiber made from cellulose, but specifically wood pulp. It is semi-synthetic due to the chemicals involved in the manufacturing process like sodium hydroxide and carbon disulfide. Similar to other cellulose fibers, viscose rayon is absorbent, breathable, and lightweight. It performed well in the thermal resistance test, however, this discrepancy could be explained by the difference in humidity between fiber measurements. (Appendix V, VI, and X)

There are a number of technical performance metrics the cellulose fabrics failed to meet ranging from low water contact angle to low tear resistance. One way to decrease the water contact angle is to treat the fabric with a hydrophobic compound. For example, incorporating betulin and betulinic acid into cellulose based fibers resulted in an increase in the water contact angle to >90° (Moriam, 2021). Similarly, the water contact angle could be improved by blending different fabrics. Other properties like tear resistance, which is a measure of the durability and strength of the fiber, and breathability could potentially be improved by blending different fabrics. For example, blending cellulose fibers like cotton that have high breathability and high hydrophilicity with synthetic fibers that tend to be more hydrophobic and have increased durability would result in fibers with new characteristics. The breaking strength of cotton fibers was improved by increasing the polyester:cotton fiber blend ratio (Manik, 2019).

### Short Chain PHAs

Polyhydroxyalkanoates (PHAs) are a family of biodegradable polyesters. They are produced by microorganisms, like bacteria, for carbon and energy storage purposes (Li, 2016). Their structural variability leads to PHAs with a variety of characteristics ranging from crystalline, stiff substrates to elastic material (Kopf, 2022). Although PHAs could be viable as a moisture barrier due to their hydrophobic nature of unmodified PHAs, one detriment of un-modified PHAs is their low thermal decomposition temperature. Modification of PHA fibers is likely required to decrease the flammability of the fiber.

Polyhydroxybutyrate (PHB) is a type of PHA we chose to investigate due to its use in polyester fiber. PHB performed well in the liquid chemical resistance test since it has a relatively high water contact angle, however, there were data gaps for water penetration resistance and thermal resistance. A value for the tear resistance was found, however it is dependent on the thickness of the fiber. (Appendix V, VI, and X)

### Graphene

Graphene is an allotrope of carbon consisting of repeated 6-membered carbon rings. This 2D material is conductive due to the repeating carbon double bonds in its structure. Investigations into graphene's applicability as a semiconductor in computer chips, biomedical sensors, and as a storage for wind and solar power are being conducted (Abdali, 2019). In addition to these applications, graphene is being investigated for its use as a fiber. Graphene can be spun into a fiber by electrospinning, a process where a liquid droplet is electrified to generate a jet and followed by the stretching of the material (Al-Dahebi, 2020). The lightweight structure and tunability via doping with various elements and functional groups of graphene lead to its applicability in textiles.

Graphene nanofibers performed average when compared to the other fibers and laminates. Although the water contact angle is above 90°, making the material hydrophobic, the compound had data gaps for thermal resistance and tear resistance. In addition, the thermal resistance and water vapor transmission were not as high as other fibers. The pore size of the material was optimal and the other properties could be improved with slight modifications. (Appendix V, VI, and X)

Other areas of concern for graphene are scalability, cost, and conductivity. Currently, graphene nanofibers and other graphene materials are synthesized on a smaller scale for biomedical sensors. The amount of material needed for a moisture barrier is orders of magnitude higher compared to a biomedical sensor. Commercially available graphene is often synthesized via chemical vapor deposition (CVD), a process where gasses react and deposit on a surface to make a graphene layer (Pistilli, 2022). This method is time consuming and costly. In addition, graphene can cost \$67,000 - \$200,000 per metric ton,

although this could be for lower quality graphene (Davis, 2020). It is important to note this cost is for graphene before nanospinning, so graphene nanofibers could be more expensive. Some work into a faster and cheaper graphene synthesis method is under investigation by researchers at Rice University. The researchers make graphene by flash Joule heating, which heats carbon-based material at high temperature for a few seconds resulting in the breaking of the chemical bonds (Davis, 2020). After heating, gasses escape and the carbon reassembles into graphene. Although more research is needed to determine the scalability of this process, it could be a viable alternative to the mass production of graphene nanofibers.

Another area of concern for graphene is the conductivity. Although conductivity is optimal for graphene when used in biosensors and other electronic devices, it could be a detriment in firefighter turnout gear (Abdali, 2019). Should firefighters come into contact with loose wires or electrified materials, a conductive fiber could lead to electrical burns. Although the moisture barrier is the middle layer of the fabric and does not come into contact with the skin, this trait should be considered moving forward.

## **Hazard Assessment**

### **Cellulose Based Fibers**

We conducted a hazard assessment on the cellulose monomer (the base of all cellulose based fibers) to serve as a proxy for the hazards associated with cellulose based fibers. The cellulose monomer is a known sensitizer-induced asthmagen in occupational settings ([AEOC](#)). This hazard is relevant in the manufacturing of cellulose based fibers; however, the risk related to asthma is essentially null once the monomer is synthesized into a fiber. Thus, the risk related to asthma is irrelevant to our firefighter population.

As cellulose is a common building material of plant cell walls, of which we frequently consume in vegetables, we determined that data gaps in our hazard assessment for cellulose are not of high concern. Thus, we consider cellulose a low risk to firefighters given that it is a biological substance and will be incorporated into a fiber.

### **Short Chain PHAs**

We conducted our hazard assessment on polyhydroxybutyrate (PHB) - a common short chain PHA - to serve as our proxy for our hazard assessment for short chain PHAs used in the synthesis of biofibers. An animal study found no association between PHB and cancer in rats, indicating a low hazard with low confidence (Peng et al. 2011). Preliminary research found a low modeled half-life of PHB in fish to be 0.504 days, suggesting low hazard with low confidence associated with aquatic toxicity. A predicted half life for PHB in soil was found to be 4.47 days and was designated a very low hazard

with high confidence ([Comptox](#)). The logKow coefficient, a proxy for bioaccumulation, for PHB was 0.31 and designated a low very hazard with high confidence ([Comptox](#)).

Even though short chain PHAs are novel, they are biopolymers produced by microorganisms and thus are projected to have few environmental and health hazards. Although there are considerable data gaps associated with short chain PHAs, we can speculate that these gaps are of limited concern.

## Graphene

We conducted our hazard assessment on graphene nanoplatelets and the graphene layer and found limited data as graphene lacks commercialization. The graphene layer is “not rapidly biodegradable” and considered “harmful to aquatic life with long lasting effects” ([ECHA](#)). However, preliminary animal studies found no skin sensitization or irritation and no eye irritation associated with graphene nanoplatelets. Additional animal studies also found no genetic toxicity. An animal study looking at the impact of repeat doses of graphene nanoplatelets through inhalation found no observed impact to rats ([ECHA](#)).

Overall, preliminary animal studies suggest low toxicity with low confidence related to Group I and II endpoints, indicating that from a hazard standpoint graphene is a viable alternative. Nonetheless, there are concerns of persistence and aquatic toxicity; however, these concerns are of less concern to firefighters once incorporated into a layer.

### *Strategy 2: Coatings*

As demonstrated above, fibers alone are not sufficient to act as a moisture barrier; either the fibers have low thermal resistance or a small water contact angle. Fire retardant coatings decrease the flammability of a fiber and, therefore, increase thermal resistance. To allow the fiber to effectively act as a moisture barrier, the coating should also increase the water contact angle and decrease reactivity of the fiber. For example, cellulose based fibers have a large number of free hydroxyl groups; these hydroxyl groups are reactive and tend to be hydrophilic, which leads to a low water contact angle. Flame retardant coatings can react with fibers by reacting with the hydroxyl groups, essentially “blocking” these sites and results in hydrophobic groups pointing away from the fiber. An example of this is shown below where Exolit 5060 PK reacts with a cellulose based fiber (figure 2).

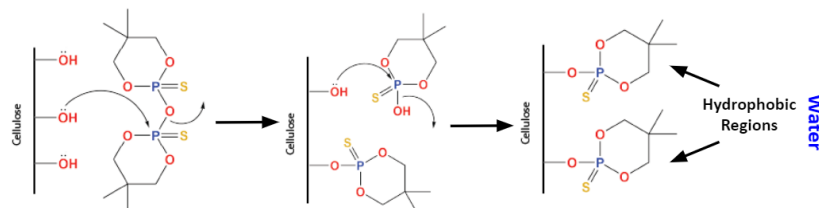


Figure 2



Silicon and phosphorus flame retardants protect fabrics by creating a protective barrier between the fabric which upon pyrolysis can produce flammable and non-flammable gasses and the heat from the flame (figure 3). Additionally, the char layer prevents oxygen gas from reacting with the fabric or flammable gasses (figure 3). The char layer forms when the phosphorus-containing compounds react with oxygen and water in the presence of heat to form a polymer like polyphosphoric acid (figure 4). It is important to note that before the char layer forms, the fiber and coating would be able to act as a moisture barrier due to the hydrophobic groups. More research needs to be conducted into at what temperature the char layer would form, which is likely dependent on the fiber-coating combination, and how long the char layer would last on the fiber.

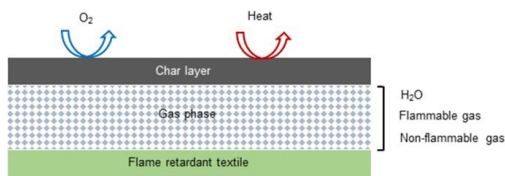


Figure 3

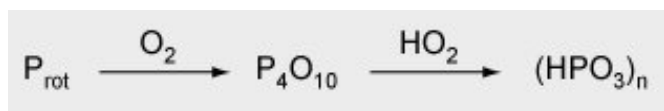


Figure 4

## Technical Performance

### Silicon Based Flame Retardants

Silicon/silicone materials have been produced commercially for over 80 years and are widely used in polymer products, construction, textiles, and electronics. One of the most common silicon materials is polydimethylsiloxane (PDMS), a polymer that is incorporated into electrical wires and cables. The stability and flame retardancy of these compounds is related to the strength of the Si-O bonds, which are inherently strong, and the flexibility of  $-\text{[Si-O]}_x-$  segments (Hamdani, 2009). When materials with silicon flame retardants are exposed to heat, they burn and leave behind an inorganic residue (char layer) that acts as a barrier to volatile, flammable gasses from the material. Silicon based flame retardants are a type of silicon material that are incorporated into textiles and building materials to decrease flammability (. We investigated three of these silicon based flame retardants, BD, BDD, and TEOS/HPDMS, as viable coatings that could enhance the moisture barrier properties of fibers.

*BD and BDD* are two novel silicon based flame retardants. These compounds are examples of schiff bases, which are commonly used in drug discovery and thermo/photochromic materials. Schiff base applications as fire retardant coatings are investigated due to their crosslinking properties and ability to form a char layer (Naik, 2015). BDD decomposed at a higher temperature than BD (Li, 2019). Although more investigation needs to be conducted into the water contact angle to determine whether this fiber-coating combination could act as a moisture barrier; the functional groups and

crosslinking ability of these compounds suggest this fire retardant/coating would be hydrophobic. (Appendix VII and XI)

*TEOS/HPDMS* performed the best of all the flame retardant coatings. The water contact angle was over 160° and the thermal decomposition temperature was the highest at 264°C. Although this number is lower than the temperature firefighters experience when combating structural fires, 300°C, it is possible that a combination of this fire retardant with another fiber would increase the thermal decomposition temperature (Lin, 2019). Although the char length was high, it was lower than the other fiber-coating combinations. This fire retardant had an optimal water contact angle and better thermal decomposition than the other silicon fire retardants and phosphorus fire retardants. (Appendix VII and XI)

### **Phosphorus Based Flame Retardants**

Phosphorus based flame retardants are currently incorporated into a variety of materials like polyethylene terephthalate (PET) fibers, polyurethane foams, furniture material, and epoxy resins (Horold, 2014). In Europe, they are being used to replace halogenated flame retardants like brominated flame retardants and polychlorinated biphenyls (Veen, 2012). Similarly, they could replace the currently brominated flame retardants in the moisture barrier. A literature analysis revealed two phosphorus flame retardants that, in addition to decreasing the flammability of the fiber, could act as moisture barriers.

Although 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is a phosphorus-containing compound incorporated into epoxy resins to decrease flammability there are little to no reports of it being incorporated into fibers. One report indicates that modification of DOPO various silicon compounds can increase fire retardancy and allow for more efficient incorporation into fibers. One example of this is 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-vinyltrimethoxysilane (DOPO-VTS), which was incorporated into cotton fibers; the results showed a flame retardant effect, however, recent efforts to modify DOPO further and create a better flame retardant are under investigation (Zhang, 2020). We investigated one of these derivatives, *DOPO-PiP-Si*, as a coating on cotton fiber. When coated onto cotton fiber, the thermal decomposition temperature was 220°C (Zhang, 2020). Even though this number is below 300°C, it is possible that a different fiber or different modification to DOPO would result in a larger decrease to fiber flammability. In addition, the water contact angle should be assessed to determine whether this fiber-coating combination could act as a moisture barrier; however, the hydrocarbon functional groups suggest this fire retardant/coating would be hydrophobic. (Appendix VII and XI)

*Exolit 5060 PK* is a phosphorus based flame retardant that is incorporated into *viscose rayon* by the chemical company Clariant (*Exolit 5060 PK*, 2022). Although there were few performance metrics reported by the company or in literature sources, this flame retardant was reported to be stable in acidic and basic media. This non-reactivity is an ideal characteristic for a moisture barrier. In addition, the fire retardant complies with fire safety standard DIN-4102-1, which is a German fire standard specific to buildings. More quantitative testing should be performed to determine its effectiveness of this fiber-coating as a moisture barrier. (Appendix VII and XI)

## **Hazard Assessment**

### **Silicon Based Flame Retardants**

For our hazard assessment of silicon based flame retardants, we looked at three chemicals used in the synthesis of novel silicon based flame retardants (FRs) BD and BDD, a chemical used in the synthesis of a novel silicon FRs, TEOS, and a chemical used in the synthesis of a novel silicon FRs HPDMS.

Two out of the three chemicals used for BD/BDD synthesis are associated with severe skin and eye damage, and one of these chemicals was found to be very toxic to aquatic life ([ECHA](#)). The other chemical was not associated with genotoxicity, skin and eye irritation, or toxicity to any organs; however, the chemical was found to be a potential skin sensitizer ([ECHA](#)). The chemical used to synthesize TEOS was found to cause skin and eye irritation, and cause damage to the respiratory tract through inhalation ([ECHA](#)). The chemical used to synthesize HPDMS was found to cause skin and eye irritation ([ECHA](#)).

Given the data gaps for these chemicals, we suggest proceeding with caution when implementing silicon based flame retardants into moisture barriers for turnout gear. Even though further research into hazards of these silicon based chemicals is recommended, we still believe that current data suggests these chemicals could be a viable alternative to PFAS in the moisture barrier. High hazards were only related to skin and eye irritation, which is less of a concern to firefighters once these reagents are synthesized into their respective silicon fire retardant.

### **Phosphorus Based Flame Retardants**

For our hazard assessment of phosphorus based flame retardants, we looked at novel FRs *Exolit 5060 PK* and DOPO, and a well-studied, non-halogenated phosphorus based pesticide Diazinon. We included this pesticide in order to provide information on the “worst case hazard scenario” for non-halogenated phosphorus chemicals and to fill in data gaps for our novel phosphorus FRs.

Preliminary animal studies on Exolit 5060 PK found no mortalities and no toxic effect related to reproductivity at the highest doses administered, indicating low hazard associated with reproductive and systemic toxicity ([ECHA](#)). Experimental studies did not find an association between Exolit 5060 PK and skin irritation or sensitization. The bioconcentration factor for Exolit 5060 PK indicates that it does not bioaccumulate; however, Exolit 5060 PK may cause long lasting harmful effects to aquatic life ([ECHA](#)). DOPO presents potential hazards, as it is toxic to aquatic life with long lasting effects and may cause an allergic skin reaction ([DK EPA](#)).

As Exolit 5060 PK and DOPO are understudied chemicals, we used well studied chemicals to inform our data gaps. Diazinon is a probable carcinogen and potential endocrine disruptor, found to be neurotoxic, and is persistent in the environment ([IARC](#), [ECHA](#), [G&L Neurotoxic](#), [OR DEQ](#)). Given these concerning hazards, we first suggest further research on novel phosphorus based flame retardants like Exolit 5060 PK and DOPO before applying them as alternatives.

### *Strategy 3: Laminates*

The laminate of the current moisture barrier consists of the bad actor chemical, ePTFE. Expanded polymers are made by incorporating a blowing agent during the manufacturing process. This blowing agent creates a cellular structure via a foaming process to materials that undergo phase transition or hardening; this creates a structure like the one in figure 5 (Ebnesajjad, 2017).

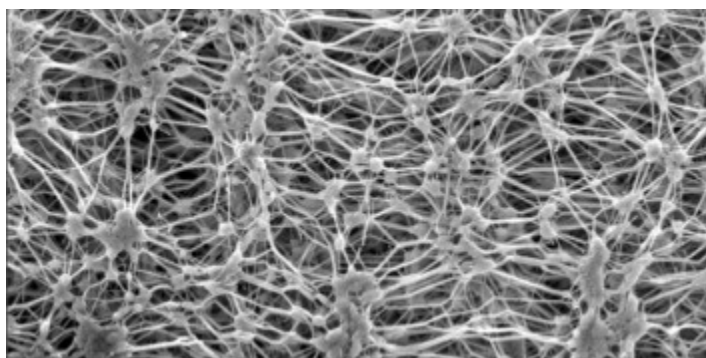


Figure 5

Expanded PTFE (ePTFE) is more porous than PTFE. The expanded polymer's increased porosity allows for airflow through the material, but prevents liquid water from penetrating the membrane (Davoudi, 2019). Similar to PTFE, other polymers like polyethylene and polyurethane, can be made into expanded polymers as well, allowing them to be applied as a laminate and employed as a moisture barrier. In fact, Gortex is looking into expanded polyethylene (ePE) membranes as an alternative to the ePTFE moisture barrier (Weigl, 2021).

## Technical Performance

### Polyethylene

Polyethylene is a polymer composed of a repeating network of carbon and hydrogens with a similar structure to PTFE. It is commonly used in chemical-resistant flooring, packaging, and containers for a variety of products. Depending on the synthesis method, high and low density polyethylene can be made (Properties and uses of polyethylene, 2022). High density polyethylene is characterized by no branches in the polymer chain, leading to a rigid material. This is why low density polyethylene is of particular interest since low density polyethylene is characterized by short and long branches in the polymer chain that prevent closed packing and lead to a flexible material. These properties as well as polyethene's low thermal conductivity make it a potential alternative to the PTFE moisture barrier.

Polyethylene performed well in two of the NFPA standard tests, the water contact angle was  $126^\circ$  and the tear resistance above the NFPA requirement. There were however some data gaps in the thermal resistance and water penetration resistance of the material. In addition, the breathability of polyethylene needs to be improved since the pore size and water vapor transmission rate were suboptimal and poor according to the rankings. (Appendix IX and XII)

### Polyurethane

Polyurethane is a polymer that was first developed in the 1930s with properties similar to rubber (Kumbasar, 2017). Over time research into polyurethane revealed that it can be modified to make foams and fine threads. It is often found as insulation in houses, floor coatings, and tires. Due to its hydrophobicity, durability, and its use as a DWR in outdoor wear, it is an ideal alternative to the ePTFE membrane.

Polyurethane has a high water contact angle of  $127^\circ$  and a similar thermal resistance to ePTFE. The breathability of polyurethane is variable based on the ranges in pore size and water vapor transmission rate (Li, 2021). In addition, there were gaps in the water vapor resistance and the tear resistance of the material. Although a value was found for the water penetration resistance, due to a difference in the test reported in the literature. (Appendix IX and XII)

## Hazard Assessment

### Polyethylene

We conducted our hazard assessment on the polyethylene (PE) polymer and the PE monomer ethylene. PE is a suspected asthmagen ([AOEC](#)) and known to be persistent in

the environment ([ECHA](#)). The monomer ethylene demonstrates evidence of carcinogenic effects but these effects were not sufficient enough to classify it as a carcinogen ([MAK](#)). Ethylene was found to be neurotoxic and may cause respiratory tract irritation through inhalation ([ECHA](#)). Additionally, ethylene was found to be harmful to aquatic life with long lasting effects ([GHS Japan](#)).

While there are potential concerns regarding health impacts related to ethylene, once ethylene is synthesized into a polymer it will pose a significantly lower risk to the firefighter population. As there are no Group I Human Endpoints associated with the polymer, and it is not likely to degrade into its monomer form, we believe PE is a viable laminate alternative to the PTFE moisture barrier. Since PE is one of the most commonly used plastics in the world and widely studied, we suspect data gaps are of limited concern rather than a gap in knowledge.

### **Polyurethane**

We conducted our hazard assessment on polyurethane (PU) polymer and two reagents used to synthesize PU - glycerol and methylene diphenyl diisocyanate. PU was found to be life-threatening at concentrations in air of 0.79 mg/L or above ([Comptox](#), [DOE PAC](#)). We assigned this concentration to be a high hazard with low confidence for acute systemic toxicity. We extrapolated this hazard level from the GreenScreen designated high hazard range for median lethal doses with the same units. The PU reagents were found to be skin and respiratory sensitizers and impact the reproductive system ([ECHA](#)). One of the reagents, methylene diphenyl diisocyanate, is suspected to be cancer causing ([ECHA](#)).

Similar to PE, there are potential concerns regarding health impacts related to the reagents used to synthesize PU. However, once these reagents are synthesized into their polymer form, they pose a significantly lower risk to the firefighter population. The polymer form does not pose risks to any Group I Endpoints, and is not likely to readily degrade into its reactants and impact our firefighting community. As PU is one of the more commonly used materials in household furnishing and has been researched for decades, hazard endpoints with data gaps are likely because studies have not indicated hazards rather than information gaps.

## **Conclusion and Recommendations**

Our alternatives were evaluated based on technical performance standards and tests we identified through our NFPA 1971 Standards critique. Fibers, flame retardant coatings, and laminates were each evaluated individually. Through our technical assessment we determined that the fibers alone are not sufficient to use as a moisture barrier, due to low water contact

angles or low thermal resistance. However, the addition of a flame retardant coating could potentially increase the water contact angle and thermal resistance based on technical assessments of the silicon and phosphorus based flame retardants, with the TEOS/HPDMS performing best with the NFPA 1971 standards. However, there were multiple data gaps in our technical assessment, and more information is needed to properly assess our alternatives as moisture barriers, specifically related to water penetration resistance. A hydrostatic pressure test could be used to further evaluate the water penetration resistance. For our laminates, the technical assessment showed that polyethylene met more NFPA 1971 standards than polyurethane, but more research is needed to further evaluate the thermal resistance.

We also evaluated our alternatives using a stepwise hazard assessment using a hazard assessment guidance document, chemical dossiers, and literature. Based on the existing literature, all three fibers appear to present low hazards and data gaps likely present little concern. Cellulose fibers may present a manufacturing risk and graphene is potentially persistent in the environment; however, all of the fibers remain as viable safer alternatives. Regarding coatings – silicon based flame retardants present a potential manufacturer risk (skin and eye irritation) and include data gaps associated with hazards for Group I Endpoints. Phosphorus based flame retardants are associated with multiple high hazards for Group I endpoints like carcinogenicity and endocrine disruption. Due to this comparative hazard, we recommend silicon based flame retardants as a safer alternative component, though its data gaps suggest further research on hazards before implementation. For laminates, both polyethylene (PE) and polyurethane (PU) reagents present moderate hazards relating to carcinogenicity and a potential manufacturer risk. Due to extensive past research on PE and PU, associated data gaps likely represent no evidence of hazards.

Considering our findings from both the technical performance and hazard assessments together, we recommend the following. Regarding the science-side of our solution, the silicon-based flame retardant coatings could be incorporated with any of the three fibers: cellulose fibers, short-chain PHAs, or graphene. Alternatively, the polyethylene laminate could be applied to one of the listed fibers. Regarding the policy-side of our solution, we advise the NFPA to drop the light degradation and viral penetration tests and keep the remaining standards. The light degradation & viral penetration tests result in an over-engineered moisture barrier and limit viable PFAS-free options. A key aspect of our challenge was to find an alternative that met these updated technical performance criteria, without making a regrettable substitution. We aimed to balance both the health hazard criteria and technical performance in determining the viability of our alternatives.

Our IAFF partners plan to continue working on this issue, and recently secured a grant to research next generation bunker gear. As previously mentioned, there is a current policy push to remove the light degradation test from the NFPA 1970 standards. Our partners talk about turnout gear daily and are working to develop safer alternatives without waiting for the NFPA to move

the needle. Through scientific innovation and improvements to outdated policy, we are excited to see a tangible shift in the safety of firefighter turnout gear.



## Appendixes

Appendix I. "Bad Actor" Hazard Assessment Table

		Group I Human Endpoints			Group II and Group II* Endpoints			Ecotoxicity	Fate	Physical Hazard
		Carcinogen./ Mutagen.	Develop./ Repro. Tox	Endocrine Activity	Systemic Toxicity	Neurotox.	Skin, Eye, Respiratory Irritation/ Sensitiz.	Aquatic Tox. Acute/ Chronic	Persist./ Bioaccumu	Reactivity, flammability
PTFE + PTFE Monomer	PTFE	M	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	vH	Data Gap
	TFE	H	vH	Data Gap	H	H	M	Data Gap	vH	H
C8s/Legacy PFAS	PFOA	H	H	H	H	H	vH	M	vH	Data Gap
	PFOS	H	H	H	H	Data Gap	M	H	vH	Data Gap
C6s/Novel PFAS	GenX	Data Gap	vH	Data Gap	M	Data Gap	vH	Data Gap	vH	L
	PFDeA/ PFDA	M	H	H	H	Data Gap	vH	Data Gap	vH	Data Gap
Brominated FR	TBBPA	H	H	H	Data Gap	Data Gap	Data Gap	vH	vH	Data Gap

Appendix II. Fibers Hazard Assessment Table

		Group I Human Endpoints			Group II and Group II* Endpoints			Ecotoxicity	Fate	Physical Hazard
		Carcinogen./ Mutagen.	Develop./ Repro. Tox	Endocrine Activity	Systemic Toxicity	Neurotoxic.	Skin, Eye, Respiratory Irritation/ Sensitiz.	Aquatic Tox. Acute/ Chronic	Persistence /Bioaccumu.	Reactivity, flammability
Cellulose (Viscose Rayon, Lyocell, Cotton, Cellulose Nanofibers)		Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	H	Data Gap	Data Gap	Data Gap
Short chain PHAs Monomers		L	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	L	vL	Data Gap
Graphene nanoplatelets		L	Data Gap	Data Gap	L	Data Gap	L	M	H	L

Appendix III: Coatings Hazard Assessment

		Group I Human Endpoints			Group II and Group II* Endpoints			Ecotoxicity	Fate	Physical Hazard
		Carcinogen./Mutagen.	Develop./Repro. Tox	Endocrine Activity	Systemic Toxicity	Neurotoxic.	Skin/Eye/Respirat Irrit./Sensitiz.	Aquatic Tox. Acute/Chronic	Persistence/Bioaccumu.	Reactivity, flammability
Silicon Flame Retardants	3,4-Dihydroxybenzaldehyde	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	H	Data Gap	Data Gap	Data Gap
	9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide	L	Data Gap	Data Gap	L	Data Gap	M	L	L	Data Gap
	1,3-Bis(3-aminopropyl)-1,1,3,3-tetraethylhydrosiloxane	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	vH	vH	Data Gap	Data Gap
	TEOS	Data Gap	L	Data Gap	vH	Data Gap	H	Data Gap	L	M
	HPDMS	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	H	Data Gap	L	Data Gap
Phosphorus Based Flame Retardants	Exolit 5060 PK	Data Gap	L	Data Gap	L	H	L	M	M	L
	DOPO	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	H	H	Data Gap	Data Gap
Phosphorus-based Pesticides	Chlorpyrifos	Data Gap	H	H	vH	H	H	vH	vH	Data Gap
	Diazinon	H	M	H	H	H	H	vH	vH	Data Gap

Appendix IV: Laminates Hazard Assessment Table

	Group I Human Endpoints			Group II and Group II* Endpoints			Ecotoxicity	Fate	Physical Hazard
	Carcinogen./Mutagen.	Develop./Repro. Tox	Endocrine Activity	Systemic Toxicity	Neurotoxic.	Skin, Eye, Respiratory Irritation/Sensitiz.	Aquatic Tox. Acute/Chronic	Persistence/Bioaccumu.	Reactivity, flammability
Polyethylene	L	Data Gap	Data Gap	Data Gap	Data Gap	M	Data Gap	vH	Data Gap
Polyethylene Monomer	M	L	Data Gap	M	H	Data Gap	M	Data Gap	H
Polyurethane	L	Data Gap	Data Gap	H	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap
Methylene Diphenyl Diisocyanate	M	M	Data Gap	H	Data Gap	H	Data Gap	Data Gap	Data Gap
Glycerol	L	M	Data Gap	M	Data Gap	H	L	Data Gap	Data Gap

Appendix V: Fibers NFPA Technical Performance Assessment

	Compound	Water Penetration Resistance	Liquid Chemical Resistance Water Contact Angle (degree)	Thermal Resistance (m <sup>2</sup> *K/W)	Tear Resistance (Newtons)
Current Fabrics	<i>Kevlar (single layer)</i>	Data Gap	61.2-66.2	0.008	3620 N/mm
	<i>Kevlar/Wool Blend (single layer)</i>	Data Gap	Data Gap	0.011	Data Gap
	<i>NOMEX</i>	Data Gap	144.7	Data Gap	113
Graphene	Graphene Nanofibers	Data Gap	95-100	0.09 m K/W	Data Gap
Cellulose Based Fabrics	Cellulose Nanofibers	Data Gap	85.9	Data Gap	Data Gap
	Lyocell (Tencel)	Data Gap	Data Gap	Data Gap	21.7168
	Cotton	Data Gap	43.9	0.01301 m K/W	22.78
	Viscose Rayon	Data Gap	Data Gap	0.189	Data Gap
Biobased Fabric	PHA/PHB fibers	Data Gap	118	Data Gap	40 N/mm

Appendix VI: Fibers Other Technical Performance Metrics

	Compound	Pore Size (diameter, μm)	Water Vapor Transmission Rate (g/(m <sup>2</sup> day))	Water Vapor Resistance (m <sup>2</sup> Pa/W)
Existing Fabric	<i>Kevlar (single layer)</i>	9.0-12.8	1815.67	9.2
	<i>Kevlar/Wool Blend (single layer)</i>	Data Gap	Data Gap	7.3
	<i>NOMEX</i>	10-100	1967.13-2151.01	2.448-2.836
Graphene	Graphene Nanofibers	0.003-0.050	848.22	Data Gap
Cellulose Based Fibers	Cellulose Nanofibers	0.02-0.3	2.46 (g/(m*s*Pa)*10 <sup>-11</sup> )	Data Gap
	Lyocell	0.001-0.1	~1000	4.42
	Cotton	Data Gap	1912.36	3.305

Appendix VII: Coatings Technical Performance Metrics

	Compound	Liquid Chemical Resistance Water Contact Angle (degree)	Thermal Decomposition (5%) Temperature (°C)	Char Length (cm)*
Phosphorus Based Flame Retardants	Viscose Rayon + Exolit 5060 PK	Stable in Acidic and Basic Solution	Data Gap	Data Gap
	Cotton + DOPO	Data Gap	220	12.2*
Silicon Based Flame Retardants	Cotton + BD	Data Gap	162	Data Gap
	Cotton + BDD	Data Gap	225	Data Gap
	Cotton + TEOS/HPDMS	>160	264	8.5*

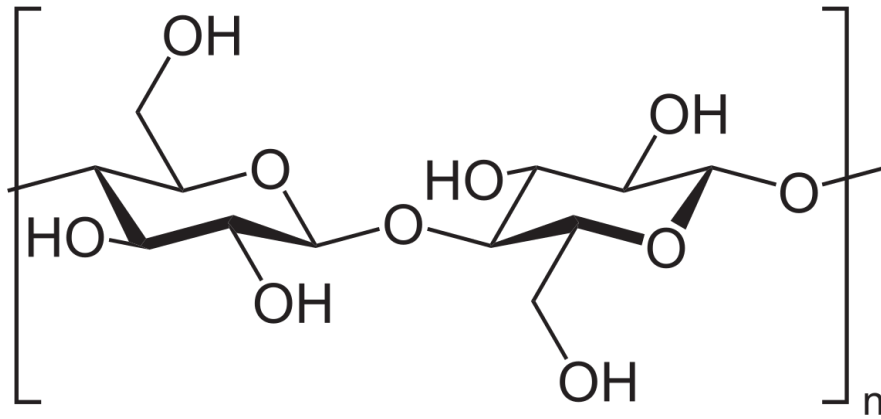
Appendix VIII: Laminates Technical Performance Metrics

Compound	Water Penetration Resistance	Liquid Chemical Resistance Water Contact Angle (degree)	Thermal Resistance (m²C/W)	Tear Resistance (Newtons)
ePTFE	Data Gap	125.5	0.0671	Data Gap
Polyurethane	1.0*10 <sup>-3</sup> -1.0*10 <sup>-4</sup> (g/mdayPa)	70, 127	0.0659	Data Gap
ePolyethylene	Data Gap	126	Data Gap	33.32

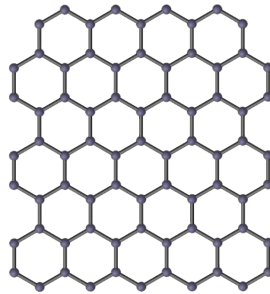
Appendix IX: Laminates Other Technical Performance Metrics

	Compound	Pore Size (diameter, µm)	Water Vapor Transmission Rate (g/(m²day))	Water Vapor Resistance (m²Pa/W)
Existing Laminate	ePTFE	0.02-10	5000-8000	Data Gap
Alternative Laminate	Polyurethane	677, 50	~1180-1500, 3960-4600	Data Gap
	Polyethylene	1-50	1.54	Data Gap

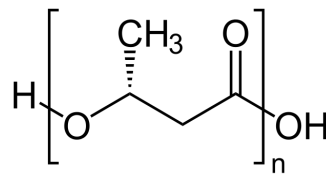
Appendix X: Structures of Fibers



**Cellulose**

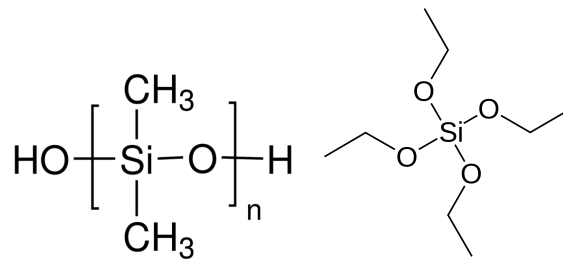


**Graphene**



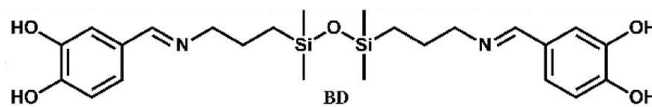
**Polyhydroxyalkoates (PHAs)**

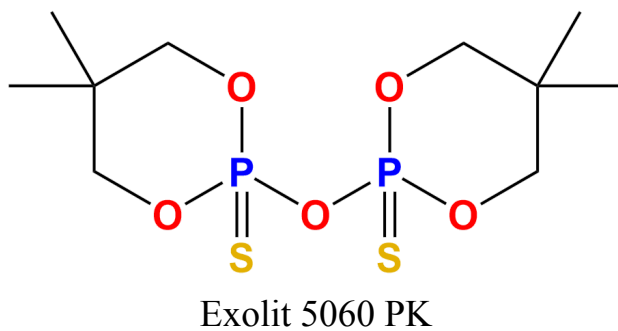
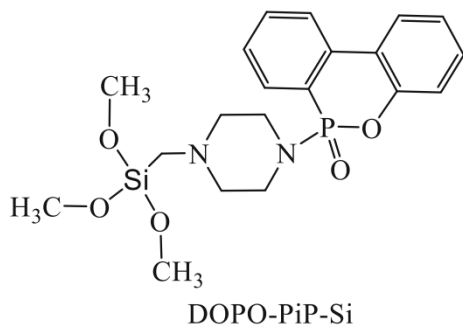
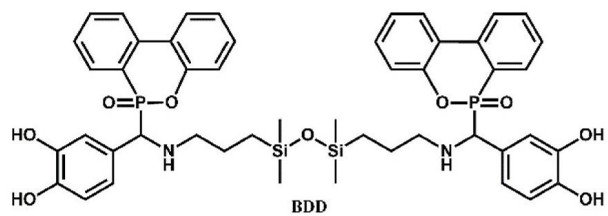
Appendix XI: Structures of Fire Retardants



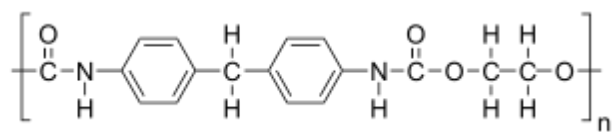
**HPDMS**

**TEOS**

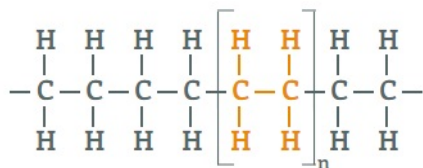




#### Appendix XII: Structures of Laminates



**Polyurethane**



**Polyethylene**

## Bio-Sketches



**Grace Campbell:** Grace is a 1st year M.S. Environmental Health Sciences student. Grace received her B.S. at UC Berkeley in Environmental Engineering Science, during which she studied the chemical remediation of PFAS in AFFF-contaminated groundwater. After receiving her Bachelor's, Grace worked for the NC State Superfund Research Center supporting PFAS research and science communication. She translated and communicated complicated PFAS research to different stakeholders, supported GenX Exposure Study, and conducted her own PFAS exposure science research. She has worked on the issue of PFAS for nearly 4 years, has a diverse knowledge of PFAS research and science, and cares deeply about working towards eliminating PFAS as a class from the entire life cycle.



**Sophia Glazer:** Sophia is a 2nd year MPH Global Health and the Environment student. Sophia is interested in the health implications of climate change. Sophia is a Research Assistant for the Sustainability and Health Equity Lab at UC Berkeley where she is researching women firefighters in San Francisco and their occupational exposures, specifically PAHs. Sophia is excited to be working with this team to share her relevant experience and knowledge and learn about/provide solutions to PFAS in firefighter turnoutgear through researching alternative materials and policies.



**Brittany Stinger:** Brittany is a 4th year Chemistry PhD candidate in the Jay Groves lab. Her current research focuses on identifying the kinetics of various proteins involved in the T-cell signaling pathway. Brittany is interested in various aspects of green chemistry, specifically related to the elimination/minimization of waste and the design of safer chemicals. Brittany is excited to lend her chemistry knowledge to this team in order to identify key issues involved with PFAS firefighter turnout gear and work towards identifying a chemical solution to PFAS in turnout gear.



**Sophie Thompson:** Sophie is a 2nd year MPH Global Health and the Environment Student. Her interests include disaster preparedness and the health implications of climate change. She has a professional background in emergency preparedness and planning along with an academic background in policy review and analysis. Sophie will be focused on the review and critique of the current NFPA standards.



**McKenna Thompson:** McKenna is a 2nd year MPH Global Health and the Environment student. For the past year she has been working with the California EPA's Office of Environmental Health Hazard Assessment to analyze air monitoring data to characterize exposures in children living in a community heavily impacted by air pollution. Her research interests center in environmental justice and the health impacts of climate change. She has a background in advocacy, policy analyses and epidemiology, and is excited to apply these skills in researching materials and standards for this challenge.



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