

Replacing PFAS In Firefighter Turnout Gear

Greener Solutions | UC Berkeley Fall 2022

The Team



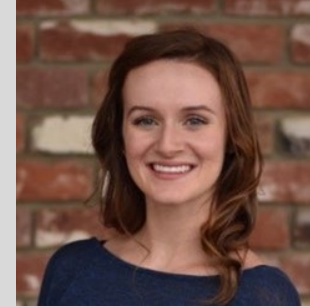
Grace Campbell
Environmental
Health Sciences
MS Candidate



Sophia Glazer
Environmental
Health Sciences
MPH Candidate



Brittany Stinger
Chemistry PhD
Candidate



McKenna Thompson
Environmental
Health Sciences
MPH Candidate



Sophie Thompson
Environmental
Health Sciences
MPH Candidate

Our Partners



Neil McMillan, Director
of Science and
Research at IAFF



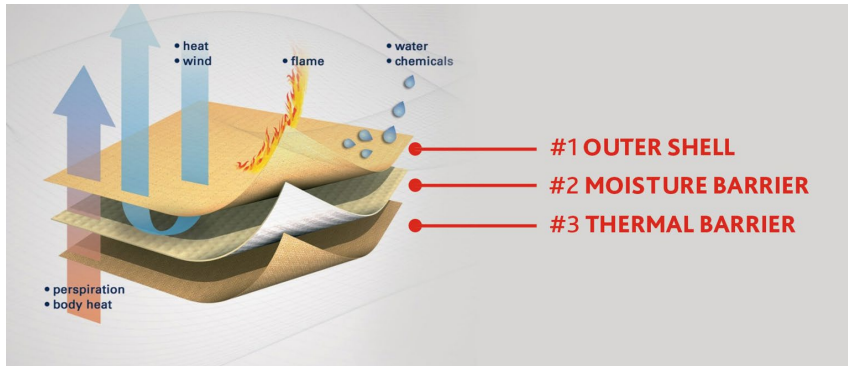
Derek Urwin, Assistant
Adjunct Professor
Chemistry & Biochemistry
at UCLA

Challenge

Find safer alternative materials that meet the required functions of the PTFE moisture barrier in firefighter turnout gear

Current Turnout Gear

Typically **3** layers in firefighter turnout gear: **Thermal Layer**, **Moisture Barrier**, **Outer Shell**



(Peeling Back the Fire Suit “Onion”, Layer #2, n.d.)

PFAS were detected in all three layers of the firefighter turnout gear. While **PTFE** is considered inert, smaller **PFAS chemicals present on firefighter turnout gear pose a risk to human and environment health.**

(Graham et al., 2020)

The **Moisture Barrier** contains a **Polytetrafluoroethylene (PTFE)** layer.

PTFE is ...

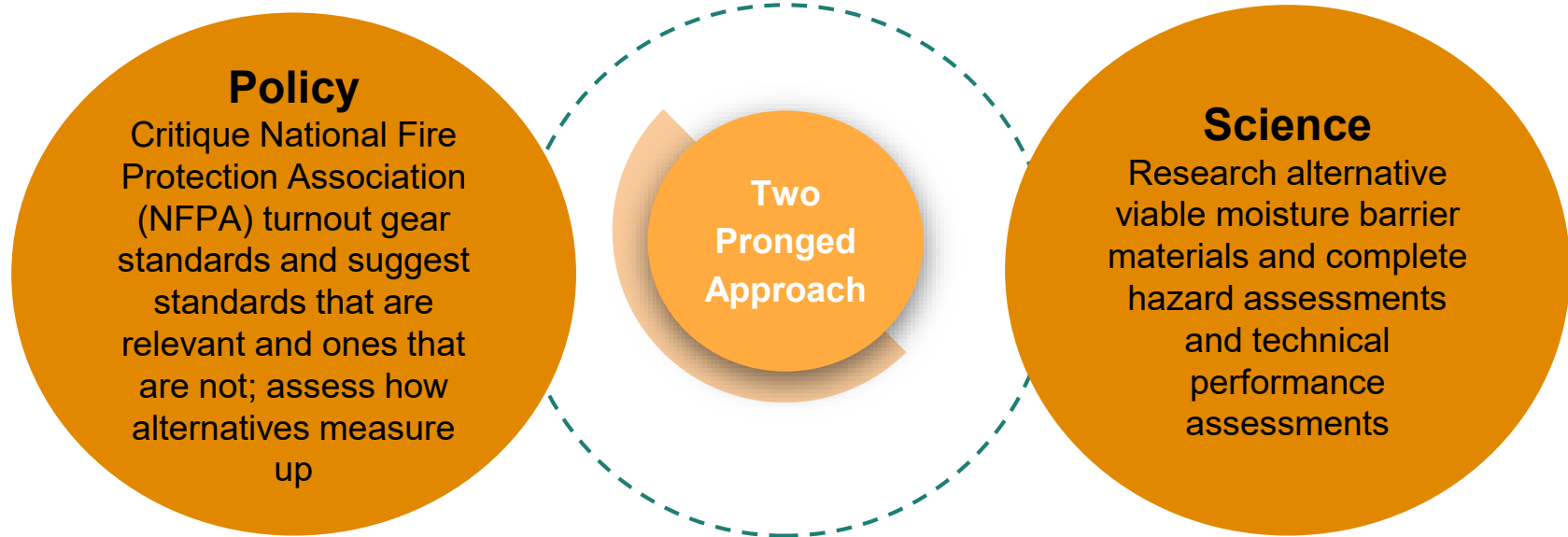
- a synthetic fluoropolymer (a polymer with multiple fluorine carbon bonds)
- one of the most well-known and applied **per- and polyfluoroalkyl substances (PFAS)** - also used in the coating of non-stick cookware.

Why does this matter?

Firefighters are disproportionately burdened by cancer

- Firefighting as an occupational exposure is considered a **Class 1 carcinogen** (IARF WHO 2022)
- The **leading cause of death in the fire services** has gone from cardiac events to cancer (IAFF)
- NIOSH reports 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).
- PFAS exposure has been **linked to multiple types of cancers**, including kidney and testicular cancer, among many other health effects (Goodrich et al., 2021)

Approach to Addressing Challenge



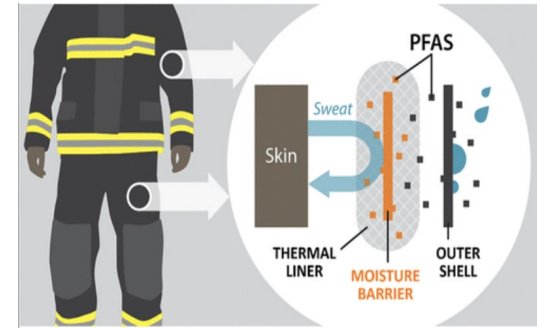
Comparison of Standards

Requirements	NFPA (US & Canada)	EN 469 - Level 2 – Structural fires (Europe)	AUS (Australia)
Heat/Thermal Resistance	Shall not shrink > 10% in any direction.	Shall not shrink >5% in any direction. No ignition. No melting.	X
Water Penetration (resistance)	Minimum water penetration resistance of 172 kPa (25 psi).	Minimum water resistance of 20 kPa	Using the rate of water pressure increase of 9.8 mbar/min and water temperature of 20 °C shall achieve ≥ 200 cm of H2O
Tear resistance	Tear strength of not less than 22 N (5 lbf).	Tear strength of no less than 30 N	Coated materials shall give a tear strength equal to or greater than 25 N
Flame Resistance	Char length <100 mm. Afterflame <2 seconds.	X	X
Cleaning Shrinkage Resistance	Cannot shrink more than 5%	Shall not shrink more than 3 % (woven) Shall not shrink more than 5% (non-woven)	At a temperature of (260 0 +5) °C, no material shall melt, drip, ignite or shrink more than 5 %
Liquid Chemical Resistance	No liquid can penetrate any sample for 1 hour	No penetration to innermost surface, index of repellency > 80%	Clothing shall give > 80 % run off with no penetration to the innermost surface
Viral Penetration Resistance	Shall allow no penetration of the Phi-X-174 bacteriophage for at least 1 hour.	X	X
Light Degradation Resistance	Water shall not appear on the surface of the specimen. *Garment is exposed to harsh light for 40 hours	X	X
Water Vapor Resistance	X	Must be less than or equal to 30 m ² Pa/W	X

NFPA Standards Critique

Light Degradation Resistance: The UV Test

- **Unnecessary** for moisture barrier: the middle layer of turnout gear does not come into contact with UV light.
- PTFE is the **only material** that meets this requirement → Removing the UV test allows for PFAS-free moisture barriers.
- May 2021, a Tentative Interim Amendment was filed by IAFF to remove UV test from the standards but NFPA denied it and subsequent appeals



(Graham et. al., 2020)

*“The UV light degradation test for moisture barriers is **illogical, not supported by science**, stands as a hurdle to advancing the state of the art in firefighter PPE”*

- IAFF TIA Appeal

*“The UV light test is stopping fire departments from moving towards procurement of PPE that doesn't contain forever chemicals. **Firefighters should be fighting fires, not NFPA and the gear companies.**”*

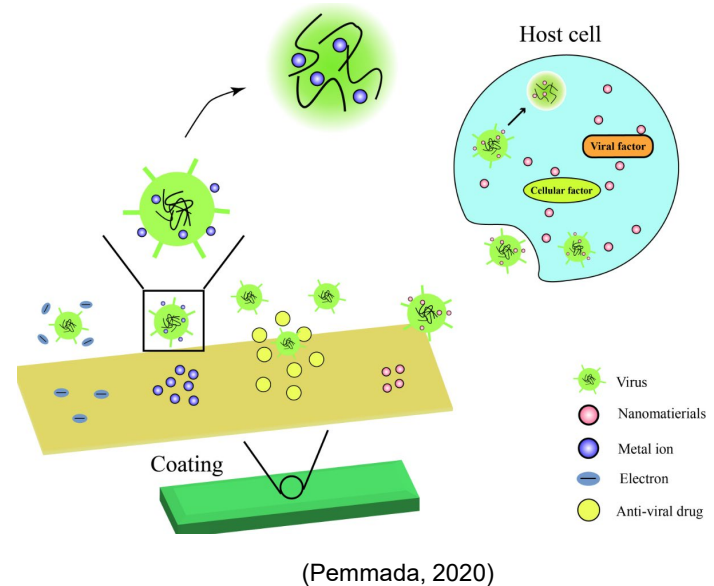
- Retired battalion chief of New Haven CT Fire Department

(Latest, n.d.)

NFPA Standards Critique

Viral penetration resistance

- **Viral penetration test** – Resistance to liquid or bloodborne pathogens
- Unnecessary for moisture barrier – an inner layer – to meet this standard
- When firefighters act in an paramedic role, they have access to other PPE (gloves, masks, etc) that do meet viral penetration standards



Technical Performance Standards

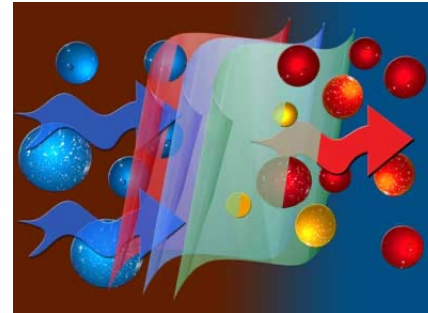
NFPA Standards:

- Heat/Thermal Resistance
- Water penetration (resistance)
- Tear resistance
- Liquid Chemical Resistance
(Water contact angle)
- Flame Resistance
- Cleaning Shrinkage Resistance



Additional Standards:

- Water Vapor Permeability
- Water Vapor Resistance
- Pore Size



Step-wise Hazard Assessment

Hazard Ranking:

Categorical = **Very High**, **High**, **Medium**, **Low**, **Very Low**

GreenScreen Guidance Doc → European Chemicals Agency (ECHA) Dossier → Literature Search

Priority Hazards/Population of Concern: Group 1 Endpoints (especially Carcinogenicity) + Firefighters

Confidence Ranking:

High Confidence = Hazard level clearly ranked in GreenScreen

Medium Confidence = Extrapolation from a range from GreenScreen (e.g. given a range of **vH-M**, chose **H**), modeled or unverified value, or extrapolated from different GreenScreen ranking entities

Low Confidence = Values (e.g. NOAELs or LD50s) provided by ECHA and compared to known values from high hazard chemicals or ECHA hazard ranking from preliminary animal studies

Hazard Assessment

“Bad Actors”

		Group I Human Endpoints			Group II and Group II* Endpoints			Ecotoxicity	Fate	Physical Hazard
		Carcinogen./ Mutagen.	Develop./ Repro. Tox	Endocrine Activity	Systemic Toxicity	Neurotoxicity	Skin, Eye, Respiratory Irritation/ Sensitiz.	Aquatic Tox. Acute/ Chronic	Persistence /Bioaccumulation	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

Major Group 1 & 2 Endpoints

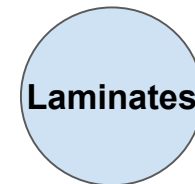
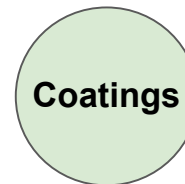
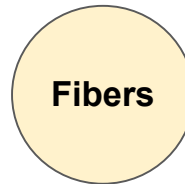
Extremely persistent

Components of the Moisture Barrier



GORE® PARALLON™ Liner System (3 Layers in this moisture barrier):

1. **Exterior Layer:** Nomex, flame resistant fabric, and a laminated ePTFE film
2. **Middle Layer:** KEVLAR/NOMEX blend and a laminated ePTFE film
3. **Body-Side layer:** KEVLAR/ NOMEX, LENZING fiber, and a laminated ePTFE film



GORE® PARALLON™ Liner System

Fibers

Cellulose Fibers



Cellulose nanofibers
Viscose Rayon
Cotton
Lyocell

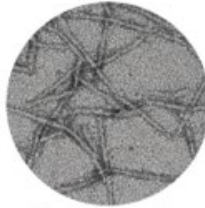
Wood

Pulp

Cellulose Nanofiber
(CNF)



Nano-fibrillation

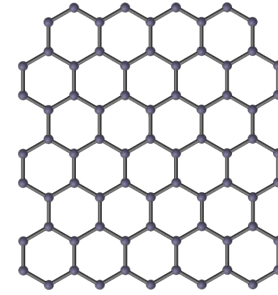


Fiber width : approx 30µm

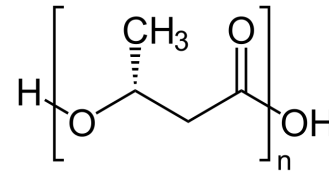
Fiber width : approx 3nm
(individualized)



Graphene



PHAs



Technical Performance Fibers

	Compound	Water Penetration Resistance
Current Fabrics	<i>Kevlar (single layer)</i>	
	<i>Kevlar/Wool Blend (single layer)</i>	
	<i>NOMEX</i>	
Graphene	Graphene Nanofibers	
Cellulose Based Fabrics	Cellulose Nanofibers	
	Lyocell (Tencel)	
	Cotton	
	Viscose Rayon	
Biobased Fabric	PHA/PHB fibers	

NFPA: >172 kPa (25 PSI)

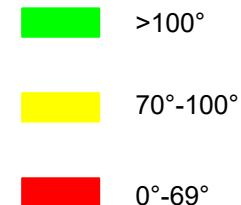
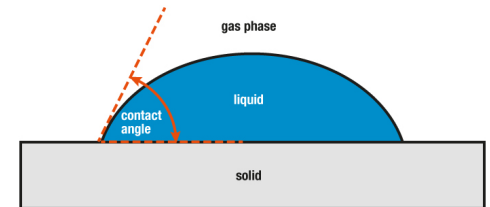
- Measures the amount of water pressure it takes to penetrate a certain distance into a fiber

 Data Gap

Technical Performance Fibers

	Compound	Water Penetration Resistance	Liquid Chemical Resistance <i>Water Contact Angle (degree)</i>
Current Fabrics	<i>Kevlar (single layer)</i>		61.2-66.2
	<i>Kevlar/Wool Blend (single layer)</i>		
	<i>NOMEX</i>		144.7
Graphene	Graphene Nanofibers		95-100
Cellulose Based Fabrics	Cellulose Nanofibers		85.9
	Lyocell (Tencel)		
	Cotton		43.9
	Viscose Rayon		
Biobased Fabric	PHA/PHB fibers		118


NFPA: No Liquid can penetrate for 1 hour




Technical Performance Fibers

NFPA: Shall not shrink >10% in any direction

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

 >0.008 m^2K/W

 <0.008 m^2K/W

Technical Performance Fibers

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

NFPA: >22N

>22N

<22N

Hazard Assessment Fibers

	Group I Human Endpoints			Group II and Group II* Endpoints			Ecotoxicity	Fate	Physical Hazard
	Carcinogen. /Mutagen.	Develop./Repro. Tox	Endocrine Activity	Systemic Toxicity	Neurotoxicity	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

Respiratory Sensitization (relevant to manufacturer exposure)

Hazard Assessment Fibers

	Group I Human Endpoints			Group II and Group II* Endpoints			Ecotoxicity	Fate	Physical Hazard
	Carcinogen./ Mutagen.	Develop./ Repro. Tox	Endocrine Activity	Systemic Toxicity	Neurotoxicity	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 PHA Monomers	L	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	L	vL	Data Gap

Biodegradable Polymer → Very Low Persistence and Bioaccumulation

Hazard Assessment Fibers

	Group I Human Endpoints			Group II and Group II* Endpoints			Ecotoxicity	Fate	Physical Hazard
	Carcinogen./ Mutagen.	Develop./ Repro. Tox	Endocrine Activity	Systemic Toxicity	Neurotoxicity	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 Monomers	L	Data Gap	Data Gap	L	Data Gap	L	M	H	L

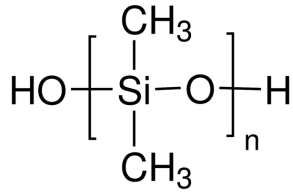
Color Scale: Lighter Color = Less Certainty!

↑
Potentially related to persistence

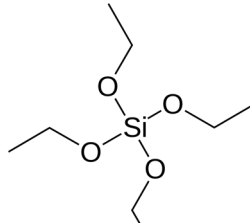
Persistent

Coatings

Silicon Flame Retardants

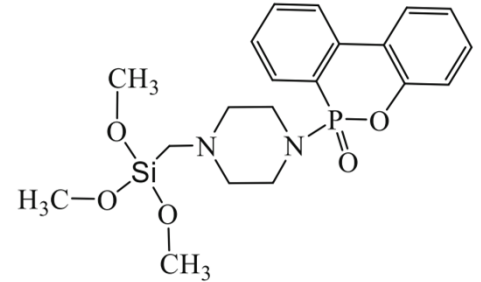


HPDMS

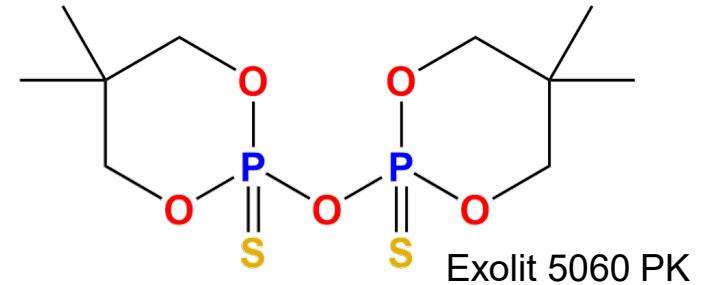
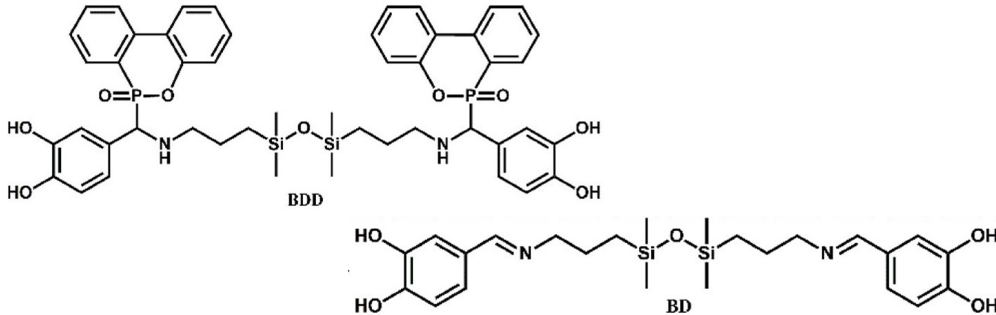


TEOS

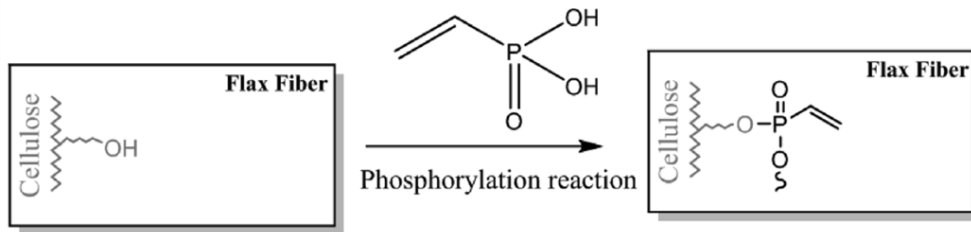
Phosphorus Flame Retardants



DOPO-PiP-Si



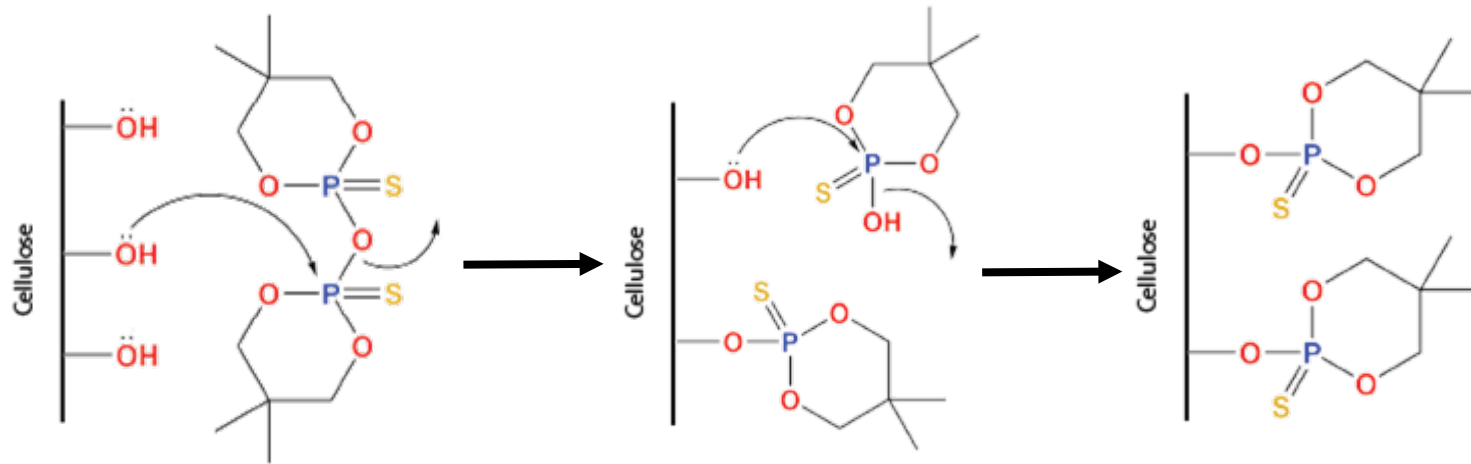
Flame Retardant Coatings are incorporated into fibers



Flame Retardant coatings are incorporated into fibers by reacting with the functional groups on the fiber.

1. Decreases flammability of the fiber
2. Potentially decreases reactivity enabling it to act as a moisture barrier

Fire Retardant Coatings are incorporated into fibers in two processes

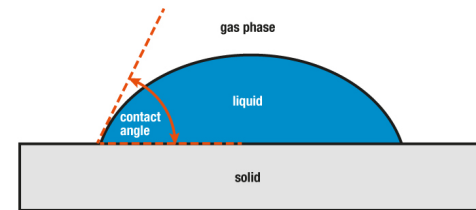


Technical Performance

Fibers + Coatings

	Compound	Liquid Chemical Resistance Water Contact Angle (degree)
Phosphorus Based Flame Retardants	Viscose Rayon + Exolit 5060 PK	Stable in Acidic and Basic Solution
	Cotton + DOPO	
Silicon Based Flame Retardants	Cotton + BD	
	Cotton + BDD	
	Cotton + TEOS/HPDMS	>160

NFPA: No Liquid can penetrate for 1 hour



>100°

70°-100°

0°-69°

Technical Performance

Fibers + Coatings

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

Technical Performance

Fibers + Coatings

	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		
	Cotton + DOPO		220	12.2*
Silicon Based Flame Retardants	Cotton + BD		162	
	Cotton + BDD		225	
	Cotton + TEOS/HPDMS	>160	264	8.5*

Hazard Assessment

Coatings

		Group I Human Endpoints			Group II and Group II* Endpoints			Ecotoxicity	Fate	Physical Hazard
		Carcinogen./ Mutagen.	Develop./ Repro. Tox	Endocrine Activity	Systemic Toxicity	Neurotoxicity	Skin/Eye/ Respirat Irrit./ Sensitiz.	Aquatic Tox. Acute/ Chronic	Persistence /Bioaccumu.	Reactivity, flammability
<p>Used to make BD & BDD</p> <p>Silicon Based Flame Retardants</p> <p>TEOS</p> <p>HPDMS</p>	}	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	H	Data Gap	Data Gap	Data Gap
		L	Data Gap	Data Gap	L	Data Gap	M	L	L	Data Gap
		Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	vH	vH	Data Gap	Data Gap
		Data Gap	L	Data Gap	vH	Data Gap	H	Data Gap	L	M
		Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	H	Data Gap	L	Data Gap

Few Group 1 Endpoints

↑
Related to
Respiratory
Irritation

↑
Skin and Eye Irritation
(less risk to firefighters)

Hazard Assessment

Coatings

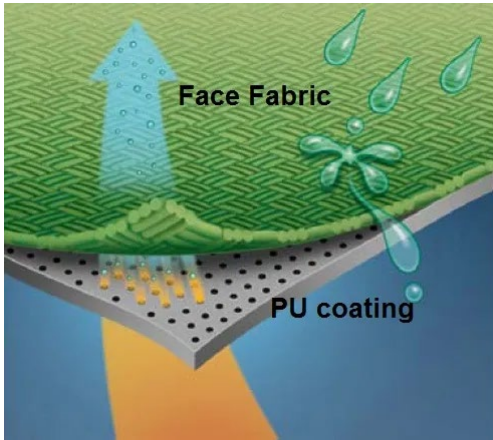
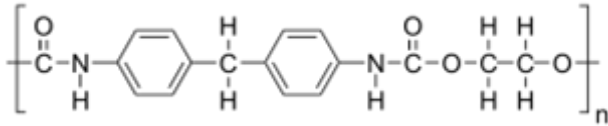
		Group I Human Endpoints			Group II and Group II* Endpoints			Ecotoxicity	Fate	Physical Hazard	
		Carcinogen./ Mutagen.	Develop./ Repro. Tox	Endocrine Activity	Systemic Toxicity	Neurotoxicity	Skin/Eye/ Respirat Irrit./ Sensitiz.	Aquatic Tox. Acute/ Chronic	Persistence /Bioaccumu.	Reactivity, flammability	
Silicon Flame Retardants		Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	H	Data Gap	Data Gap	Data Gap	
		L	Data Gap	Data Gap	L	Data Gap	M	L	L	Data Gap	
		Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	vH	vH	Data Gap	Data Gap
		Data Gap	L	Data Gap	vH	Data Gap	Data Gap	H	Data Gap	L	M
		Data Gap	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 (Novel Phosphorus FR)	Data Gap	Data Gap	Data Gap	Data Gap	Data Gap	H	H	Data Gap	Data Gap	
	Two phosphorus based pesticides	Data Gap	H	H	vH	H	H	vH	vH	Data Gap	
		H	M	H	H	H	H	vH	vH	Data Gap	

Data gaps for Novel
Phosphorus FRs

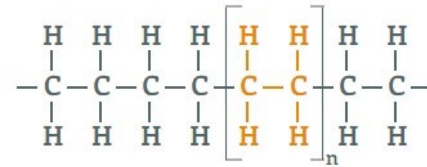
Major Group 1 & 2 Endpoints for phosphorus
based pesticides = worst case health scenario

Laminates

Polyurethane











Polyethylene



Technical Performance Laminates

Compound	Water Penetration Resistance	Liquid Chemical Resistance Water Contact Angle (degree)	Thermal Resistance (m ² C/W)	Tear Resistance (Newtons)
ePTFE		125.5	0.0671	
Polyurethane	1.0*10 ⁻³ -1.0*10 ⁻⁴ (g/mdayPa)	70	0.0659	
ePolyethylene		126		33.32

NFPA

>172 kPa (25 PSI)	 >100°	 >0.008 m ² K/W	 >22N
	 70°-100°	 <0.1 mK/W	 <22N
	 0°-69°	 <0.008 m ² K/W	

Hazards Assessment

Laminates

	Group I Human Endpoints			Group II and Group II* Endpoints			Ecotoxicity	Fate	Physical Hazard
	Carcinogen./ Mutagen.	Develop./ Repro. Tox	Endocrine Activity	Systemic Toxicity	Neurotoxicity	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

Potential Group 1 Endpoints

Neurotoxicity

Persistent synthetic polymer

Hazards Assessment

Laminates

	Group I Human Endpoints			Group II and Group II* Endpoints			Ecotoxicity	Fate	Physical Hazard
	Carcinogen./ Mutagen.	Develop./ Repro. Tox	Endocrine Activity	Systemic Toxicity	Neurotoxicity	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	Data Gap	Data Gap	H	Data Gap	Data Gap	Data Gap
Polyurethane Monomers	M	M	Data Gap	H	Data Gap	H	Data Gap	Data Gap	Data Gap
	L	M	Data Gap	M	Data Gap	H	L	Data Gap	Data Gap

Potential Group 1 Endpoints






Associated with respiratory system →
Not major firefighter risk

Skin and Respiratory
Sensitization

Additional Performance Metrics

Fibers + Laminates

Pore Size: Distance between two sides of a pore

-  >0.004 and <1
-  >1 and <100
-  >100

Water Vapor (0.0004 μ m)
Liquid Water (1-100 μ m)

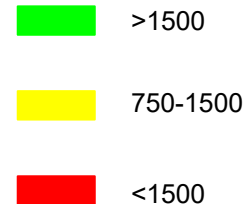
	Compound	Pore Size (diameter, μ m)
<i>Existing Fabric</i>	<i>Kevlar (single layer)</i>	9.0-12.8
	<i>Kevlar/Wool Blend (single layer)</i>	
	<i>NOMEX</i>	10-100
Graphene	Graphene Nanofibers	0.003-0.050
Cellulose Based Fibers	Cellulose Nanofibers	0.02-0.3
	Lyocell	0.001-0.1
	Cotton	

<i>Existing Laminate</i>	<i>ePTFE</i>	0.02-10
Alternative Laminate	Polyurethane	677
	Polyethylene	1-50

Additional Performance Metrics

Fibers + Laminates

Water Vapor Transmission Rate: The rate at which water vapor passes through a fiber or membrane at a certain humidity.



	Compound	Pore Size (diameter, μm)	Water Vapor Transmission Rate ($\text{g}/(\text{m}^2\text{day})$)
Existing Fabric	<i>Kevlar (single layer)</i>	9.0-12.8	1815.67
	<i>Kevlar/Wool Blend (single layer)</i>		
	<i>NOMEX</i>	10-100	1967.13-2151.01
Graphene	Graphene Nanofibers	0.003-0.050	848.22
Cellulose Based Fibers	Cellulose Nanofibers	0.02-0.3	$2.46 (\text{g}/(\text{m}^*\text{s}*\text{Pa})*10^{-11})$
	Lyocell	0.001-0.1	~1000
	Cotton		1912.36

Existing Laminate	ePTFE	0.02-10	5000-8000
Alternative Laminate	Polyurethane	677	~1180-1500, 3960-4600
	Polyethylene	1-50	1.54

Additional Performance Metrics

Fibers + Laminates

EN (Europe)
<30 m²Pa/W

 <30

 >30

	Compound	Pore Size (diameter, μm)	Water Vapor Transmission Rate (g/(m ² day))	Water Vapor Resistance (m ² Pa/W)
Existing Fabric	<i>Kevlar (single layer)</i>	9.0-12.8	1815.67	9.2
	<i>Kevlar/Wool Blend (single layer)</i>			7.3
	<i>NOMEX</i>	10-100	1967.13-2151.01	2.448-2.836
Graphene	Graphene Nanofibers	0.003-0.050	848.22	
Cellulose Based Fibers	Cellulose Nanofibers	0.02-0.3	2.46 (g/(m*s*Pa)*10 ⁻¹¹))	
	Lyocell	0.001-0.1	~1000	4.42
	Cotton		1912.36	3.305
Existing Laminate	<i>ePTFE</i>	0.02-10	5000-8000	
Alternative Laminate	Polyurethane	677	~1180-1500, 3960-4600	
	Polyethylene	1-50	1.54	

Conclusions and Recommendations

Technical Assessment

Fibers

Cellulose Fibers

Meets Tears Resistance
Low Water Contact angle

Short Chain PHAs

High Water Contact Angle
Data Gaps

Graphene

Low Water Contact Angle
Low Thermal Resistance

Coatings

Silicon Based Flame Retardants

Increase Water Contact Angle
Data Gaps

Phosphorus Based Flame Retardants

Increase Thermal
Decomposition Temperature
Data Gaps

Laminates

Polyethylene

High Water Contact Angle
Data Gaps on Thermal Resistance

Polyurethane

Low Water Contact Angle
Meets other standards

Conclusions and Recommendations

Hazard Assessment

Fibers

Cellulose Fibers

Manufacturing Risk
Data Gaps

Short Chain PHAs

Biodegradable
Data Gaps

Graphene

Concerns of Persistence
Data Gaps

Coatings

Silicon Based Flame Retardants

Few Group 1 Endpoints
Potential Manufacturer Risk

Phosphorus Based Flame Retardants

Many Group 1 Endpoints
Data Gaps for Novel PFRs

Laminates

Polyethylene

Monomer Potential Carcinogen
Polymer Persistence

Polyurethane

Monomer Potential Carcinogen
Potential Manufacturer Risk

Conclusions and Recommendations

Science Recommendations

Fibers

Cellulose Fibers
Short Chain PHAs
Graphene



Coatings

Silicon Based
Flame Retardants



Laminates

Polyethylene

Policy Recommendations

- We advise the NFPA to *drop the light degradation and viral penetration tests* and keep those that remain.
 - Light degradation & viral penetration tests result in over-engineered moisture barrier
 - Standards are limiting viable PFAS-free options

Remaining Questions

- We evaluated each of our science strategies (fabrics, fabrics/coatings, laminates) separately, but would combining all three of these produce a better moisture barrier, enhance moisture barrier properties?
- Although phosphorus and silicon based flame retardants could be used in the moisture barrier, they could pose other health hazards to firefighters; data gaps
- How do we balance the health hazards and technical performance in our assessment of the viability of these alternatives?
- Although data gaps exist, our three strategies offer novel suggestions that advance the field of occupational firefighter health

References

- Ahn, C., Yoo, H. J., Oh, Y., Han, S., Lee, H., Kim, J. H., Song, K. Rhie, J. S. Evaluating the Physical and Fabric Hand Characteristics of Lyocell Fabrics Made with Different Wood Pulp. *Textile Research Journal*, 2015. <https://pubs.acs.org/doi/full/10.1021/la304645w>
- Aidani, R., Nguyen-Tri, P., Malajati, Y. Lara., J., and Vu-Khanh, T. [Photochemical aging of an e-PTFE/NOMEX® membrane used in firefighter protective clothing](https://doi.org/10.1016/j.polymdegradstab.2013.04.002). *Polymer Degradation and Stability*, 2013. <https://doi.org/10.1016/j.polymdegradstab.2013.04.002>
- Australian Standard. (n.d.) *Protective clothing for firefighters—Requirements and test methods for protective clothing used for structural firefighting*.
- Bhattacharjee, S., et al. [“Graphene Modified Multifunctional Personal Protective Clothing”](https://doi.org/10.1016/j.compositesb.2019.03.001) *Adv Mater Interfaces*. 6(21) (2019).
- Daniels, R. D., Kubale, T. L., Yiin, J. H., Dahm, M. M., Hales, T. R., Baris, D., Zahm, S. H., Beaumont, J. J., Waters, K. M., & Pinkerton, L. E. (2014). Mortality and cancer incidence in a pooled cohort of US firefighters from San Francisco, Chicago and Philadelphia (1950–2009). *Occupational and Environmental Medicine*, 71(6), 388–397. <https://doi.org/10.1136/oemed-2013-101662>
- Demers, P. A., DeMarini, D. M., Fent, K. W., Glass, D. C., Hansen, J., Adetona, O., Andersen, M. H., Freeman, L. E. B., Caban-Martinez, A. J., Daniels, R. D., Driscoll, T. R., Goodrich, J. M., Graber, J. M., Kirkham, T. L., Kjaerheim, K., Kriebel, D., Long, A. S., Main, L. C., Oliveira, M., ... Schubauer-Berigan, M. K. (2022). Carcinogenicity of occupational exposure as a firefighter. *The Lancet Oncology*, 23(8), 985–986. [https://doi.org/10.1016/S1470-2045\(22\)00390-4](https://doi.org/10.1016/S1470-2045(22)00390-4)
- European Standards. (n.d.). *Protective Clothing for Firefighters - Performance requirements for protective clothing for firefighter activities*. BSI Standards Limited - EN 469:2020.
- Fire Fighter Cancer Awareness Month—IAFF*. (n.d.). Retrieved October 24, 2022, from <https://www.iaff.org/cancer-awareness-month/>
- Goodrich, J. M., Calkins, M. M., Caban-Martinez, A. J., Stueckle, T., Grant, C., Calafat, A. M., Nematollahi, A., Jung, A. M., Graber, J. M., Jenkins, T., Slitt, A. L., Dewald, A., Cook Botelho, J., Beitel, S., Littau, S., Gulotta, J., Wallentine, D., Hughes, J., Popp, C., & Burgess, J. L. (2021). Per- and polyfluoroalkyl substances, epigenetic age and DNA methylation: A cross-sectional study of firefighters. *Epigenomics*, 13(20), 1619–1636. <https://doi.org/10.2217/epi-2021-0225>
- Islam, M. S., and van de Ven, T. G. M. (2021). [“Cotton-based flame-retardant textiles: A review.”](https://doi.org/10.1002/biot.3911) *BioResources* 16(2), 4354-4381.
- Kuang, P. and Constant, K. [Increased Wettability and Surface Free Energy of Polyurethane by Ultraviolet Ozone Treatment](https://doi.org/10.1016/j.jcis.2014.05.001). 2014. DOI: 10.5772/60798.
- Latest action on firefighting PPE standard underscores the need to better understand and to participate in the standards process | NFPA | NFPA*. (n.d.). Retrieved December 5, 2022, from <https://www.nfpa.org/News-and-Research/Publications-and-media/Blogs-Landing-Page/NFPA-Today/Blog-Posts/2021/11/05/Latest-action-on-firefighting-PPE-standard-underscores-the-need-to-better-understand>
- Li, K. Clarkson, C. et al. [“Alignment of Cellulose Nanofibers: Harnessing Nanoscale Properties to Macroscale Benefits”](https://doi.org/10.1021/acs.nanolett.1c01111) *ACS Nano* 15, 3, 3646-3673 (2021).
- Li, N., Ming, J. et al. [“Novel Eco-Friendly Flame Retardants Based on Nitrogen-Silicone Schiff Base and Application in Cellulose”](https://doi.org/10.1021/acs.suschemeng.9b05338) *ACS Sustainable Chem. Eng.* 2020, 8, 290-291. DOI: 10.1021/acsuschemeng.9b05338
- Lin, D. Zeng, X. Li, H., Lai, X. and Wu, T. [One-pot fabrication of superhydrophobic and flame-retardant coatings on cotton fabrics via sol-gel reaction](https://doi.org/10.1016/j.jcis.2018.08.060). *Journal of Colloid and Interface Science*, 2019. <https://doi.org/10.1016/j.jcis.2018.08.060>
- Ma, H., Burger, C. Hsiao, B. and Chu, B. [Ultra-fine Cellulose Nanofibers: New Nano-scale Materials for Water Purification](https://doi.org/10.1021/ja10111a001). *Journal of Materials Chemistry*, 2011.
- Mahbub, R. F., Wang, L. Arnold, L., Kaneslingam, S. Padhye, R. Thermal Comfort Properties of Kevlar and Kevlar/wool fabrics. 2014. <https://doi.org/10.1177/00405175145321>

References

- National Fire Protection Association. (2018). NFPA 1971: Standard on Protective Ensembles for Structural Firefighting and Proximity Firefighting.
- Nechyporchuk, O. Bordes, R. Kohnke, T. [Wet Spinning of Flame-Retardant Cellulosic Fibers Supported by Interfacial Complexation of Cellulose Nanofibrils with Silica Nanoparticles](#). *ACS Appl. Mater. Interfaces* 2017, 9, 44, 39069–39077. <https://doi.org/10.1021/acsami.7b13466>
- Peaslee, G. F., Wilkinson, J. T., McGuinness, S. R., Tighe, M., Caterisano, N., Lee, S., Gonzales, A., Roddy, M., Mills, S., & Mitchell, K. (2020). Another Pathway for Firefighter Exposure to Per- and Polyfluoroalkyl Substances: Firefighter Textiles. *Environmental Science & Technology Letters*, 7(8), 594–599. <https://doi.org/10.1021/acs.estlett.0c00410>
- Peeling back the fire suit “onion”, layer #2: The moisture barrier. (n.d.). Retrieved December 5, 2022, from <https://eu.tencatefabrics.com/blog/fire-suit-layer-moisture-barrier>
- Pemmada, R., Zhu, X., Dash, M., Zhou, Y., Ramakrishna, S., Peng, X., Thomas, V., Jain, S., & Nanda, H. S. (2020). Science-Based Strategies of Antiviral Coatings with Viricidal Properties for the COVID-19 Like Pandemics. *Materials*, 13(18), Article 18. <https://doi.org/10.3390/ma13184041>
- *PFAS Exposure and Risk of Cancer—NCI* (nciglobal.ncicenterprise). (2020, October 15). [CgvArticle]. <https://dceg.cancer.gov/research/what-we-study/pfas>
- *Potential health effects of PFAS chemicals* | ATSDR. (2022, September 9). <https://www.atsdr.cdc.gov/pfas/health-effects/index.html>
- Standards Australia Limited 2019. (2019, June 25). Protective clothing for firefighters — Requirements and test methods for protective clothing used for structural firefighting.
- Sun, Y., Chen, W. and Zhou, X. [Thermal insulation fibers with a Kevlar aerogel core and a porous Nomex Shell](#). *Royal Society of Chemistry*, 2021. DOI: 10.1039/d1ra06846f
- Suzuki, M., Tachibana, Y., and Kasuya, K. [“Biodegradability of poly\(3-hydroxyalkanoate\) and poly\(ε-caprolactone\) via biological carbon cycles in marine environments”](#) *Polymer Journal*. 53, 47-66 (2021).
- Taherian, F., Marcon, V., van der Vegt, N. and Leroy, F. [What is the Contact Angle of Water on Graphene?](#) *Langmuir*, 2013, 29, 5, 1457-1465. <https://doi.org/10.1021/la304645w>
- Ting-Ting Li, Peiyao Liu, Hongyang Wang, Wenna Dai, Jie Wang, Zhike Wang, Bing-Chiuan Shiu, Ching-Wen Lou, Jia-Horng Lin. Preparation and characteristics of flexible polyurethane foam filled with expanded vermiculite powder and concave-convex structural panel. *Journal of Materials Research and Technology*, 2021. <https://doi.org/10.1016/j.jmrt.2021.03.045>
- Velencoso, M., Bating, A. Markwart, J. et. al. [“Molecular Firefighting - How Modern Phosphorus Chemistry Can Help Solve the Challenge of Flame Retardancy”](#) *Angewandte Chemie*, 57, 33 10450-10467 (2018).
- Wang, S., Chen, W. Xiang, H. et. al. [“Modification and Potential Application of Short-Chain-Length Polyhydroxyalkanoate \(SCL-PHA\)”](#) *Polymers*, 8(8), 273 (2016).
- W. Patrick Arnott, Carl Schmitt, Yangang Liu, and John Hallett, [“Droplet size spectra and water-vapor concentration of laboratory water clouds: inversion of Fourier transform infrared \(500–5000 cm⁻¹\) optical-depth measurement,”](#) *Appl. Opt.* 36, 5205-5216 (1997) <https://opg.optica.org/ao/abstract.cfm?URI=ao-36-21-5205>
- Weil, E. and Levchik, S. “Phosphorus Flame Retardants” (2017) <https://doi.org/10.1002/0471238961.1608151923050912.a01.pub3>
- Gong, C., He, Y., Znhou, J. Chen, W. Han, W. Zhang, Z., Zhang, P., Pan, X. Zhiguang, W. and Xie, E. [Synthesis on Winged Graphene Nanofibers and Their Electrochemical Capacitive Performance](#). *ACS Appl. Mater. Interfaces* 2014, 6, 17, 14844–14850. <https://doi.org/10.1021/am5016167>
- Zhang, Z., Dong, C., Liu, J. Kong, D., Sun, L. and Lu, Z. [Preparation of a synergistic reactive flame retardant based on silicon, phosphorus and nitrogen and its application to cotton fabrics](#). *Cellulose* 27, 1799-1815 (2020)