Firefighter's Clothing and Equipment : Performance, Protection and Comfort

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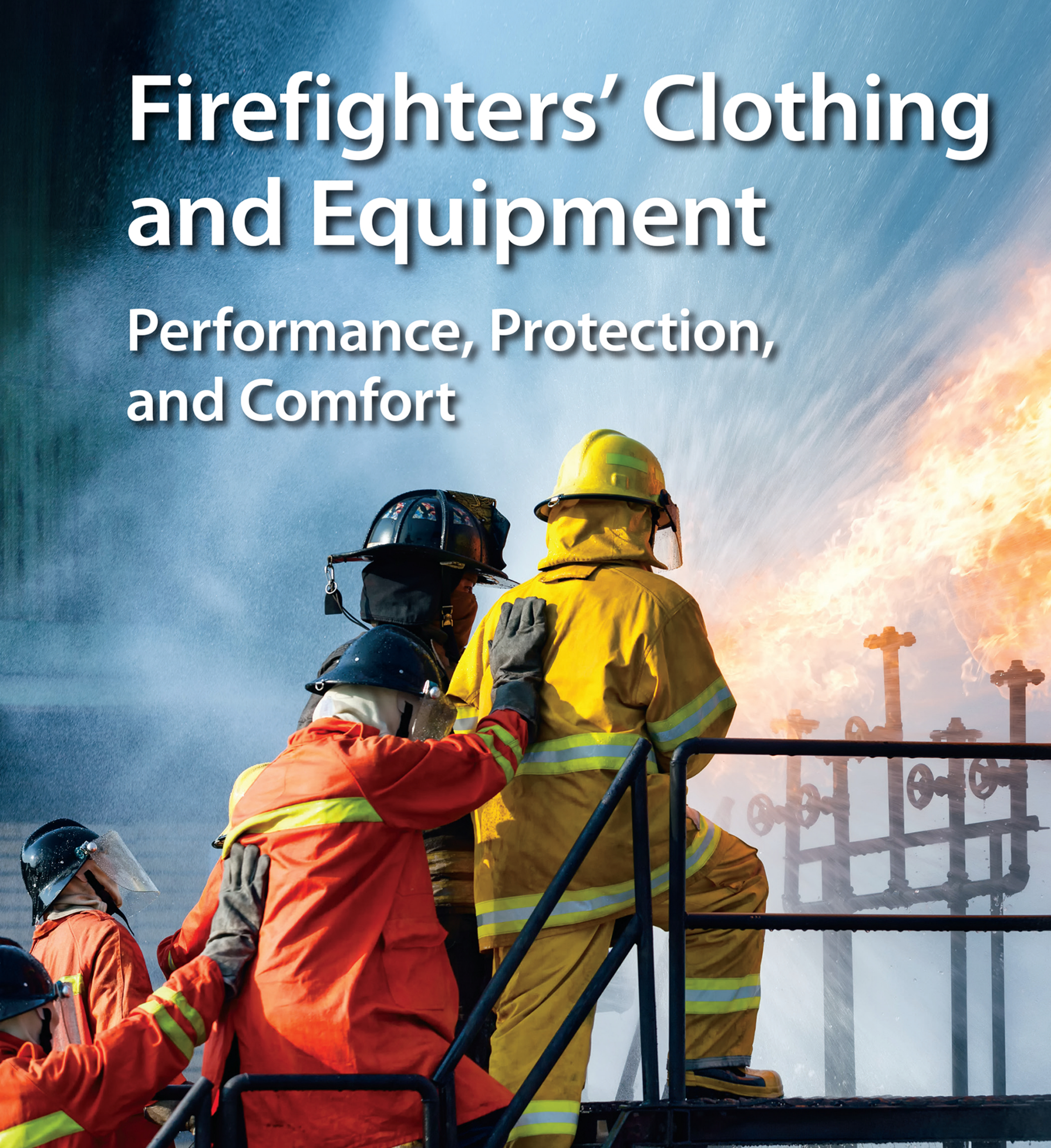

Firefighters' Clothing and Equipment

Performance, Protection, and Comfort

Edited by
Guowen Song
Faming Wang

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Preface

Personal protective equipment (PPE) and textile-based equipment are critical for firefighters to ensure their safety and health. Ineffective protection at a fire scenario with multiple hazards can cause injury and fatality as well as potentially increase property damage and loss. Fire reports [1] confirm that in the past four decades in the United States about 68,000 firefighters received burn injuries with more than 60 fatalities each year. The best approach for firefighters to mitigate burn injuries and reduce risk of death from unpredictable hazards is to apply high-performance PPE.

Firefighters encounter complex environments and conditions while performing their duties within a wide range of possible hazards. Thermal exposure, which may result from radiation, convection, hot liquid, steam, and/or hot solids, is the primary possible hazard exposure for firefighters. During combustion of structural materials, firefighters can encounter thermal hazards including collapsing fireground debris, hot liquid, and molten materials. In a fire scene, cool water from a hose can quickly become hot water, and then steam. Steam and wet air cause more serious burns because more heat energy can be stored in water vapor than in dry air. On the other hand, in some geographic regions, severe winter weather with sub-zero temperatures poses cold injury threats such as frostbite to firefighters, especially when the PPE system gets wet by sweat or hose water.

Current firefighter protective ensembles are heavy and stiff and suffer from reduced vapor permeability, all of which increase physiological strain. Statistics showed that overexertion, physical and thermal stresses, and medical issues account for 42% of the main causes of deaths. PPE are engineered with not only increased thermal protection but also increased bulk and weight. This affects efficiency and mobility, increasing the metabolic cost of work by up to 50% [2]. Furthermore, the fabric thickness and moisture barrier layers restrict body heat dissipation and create additional undue heat stress. The heat generated from working muscles, as well as the heat transferred from the local environment, generate increased thermoregulatory strain, putting more demand on the cardiovascular system. Uncompensated heat strain will greatly affect the performance, function, and health of the firefighters.

The current system tends to store large amounts of thermal energy during exposure to fire hazards, and this amount of stored energy can be discharged to the skin. Studies [3–5] have demonstrated that stored thermal energy contributes significantly to skin burn injuries, specifically compression burns. As a result, firefighters' arms and legs, knees, elbows, and shoulders, where SCBA (self-contained breathing apparatus) straps press the surrounding fabric against the skin, are vulnerable to burn injuries from stored energy discharge by compression. This compress burn actually relates to another major issue of concern for firefighters on their ability to sense the heat of the fire.

Additionally, existing product standards and testing protocols are not adequately developed to evaluate the risks caused by those hazards when combined with moisture on performance. During firefighting, protective clothing becomes wet from internal and external sources. At a high ambient temperature or during strenuous activity, the wearer perspires profusely, so clothing next to the skin becomes saturated with perspiration. Studies [6,7] show that the presence and distribution of moisture have a complex effect on heat transfer through insulating materials. In some occasions, if water vapor transfers to the human skin and condenses, steam burns may occur, as the water vapor also transfers the heat it absorbed to evaporate.

The core challenges for current PPE used for firefighters are the engineering and design of multifunctional performance for the high-level protection with minimum physiological burdens. The solution for this relies on the next-generation new textile materials, new discoveries on functional design and novel technology, as well as the understanding on mechanisms associated with heat and mass transfer in the human-clothing-environment system.

With this goal, we have developed this volume that presents an overview of the current state of understanding and knowledge for protective clothing and equipment, as well as issues and challenges associated with firefighter and other emergency first responders. This book includes 12 chapters and covers discussion on textile materials, clothing comfort and protective performance, human thermoregulation system, relevant methods and standards, instrumentation technologies for comfort and protection, 3D body scanning application, and human trials. In addition, future trends on smart firefighting clothing/equipment and numerical modeling and human skin burn are also presented.

We sincerely hope our efforts on this book will provide useful information and the present knowledge regarding hazards, firefighters, and protective clothing and equipment. This book may serve as a useful tool and technical source for scientists in textiles and clothing, mechanical engineering, and occupational safety and health. It is also our expectation that the book will provide a fundamental guide to educators, engineers, ergonomists, industrial hygienists, and designers in universities, research institutes, fire stations, and industrial companies.

We would like to express our sincere appreciation to all the authors and guest reviewers who devoted considerable effort to this book. We would also like to extend our thanks to the production team at Taylor & Francis for their patience with the editors and authors.

Guowen Song
Faming Wang
April 2018

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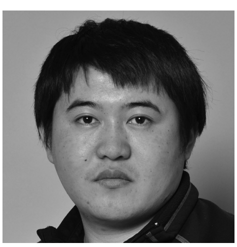
Editors

Guowen Song received his PhD degree in textile engineering, chemistry, and science at North Carolina State University's College of Textiles in Raleigh, North Carolina. Currently he is the Noma Scott Lloyd Chair in the Department of Apparel, Event and Hospitality Management (AESHM) at Iowa State University's College of Human Sciences. Song's academic interest is in functional textile materials, protective clothing, and systems to improve human health and safety. His work involves modeling studies of human physiology, textile materials, and protective clothing, development of devices and test protocols, and analysis of textile and clothing performance. His current focus is to establish a unique, multifaceted, cross-disciplinary research and education program that can integrate theoretical study, new technology discovery, and engineering with the aim of revolutionizing clothing system function and performance. These studies include lab simulations, application of instrumented manikin technology, and specially designed human trials, including 3D body scanning, and a human motion analysis approach. Dr. Song has published more than 100 scientific papers in peer-reviewed journals and conference proceedings. He authored several books and contributed a dozen chapters to books in his field of study.



Faming Wang is currently an assistant professor in clothing technology at the Institute of Textiles and Clothing (ITC) of The Hong Kong Polytechnic University. He earned his LicPhil and PhD degrees from Lund University (Sweden) under the supervision of world-renowned physiologist Professor Ingvar Holmér. After his PhD training, Dr. Wang joined Eidgössische Materialprüfungs-und Forschungsanstalt (EMPA Swiss Federal Laboratories for Materials Science and Technology, the ETH Domain, Switzerland) as a Marie-Curie Fellow. He later became a full professor (the youngest full professor in textiles and clothing in the history of Mainland China) in apparel design and engineering at Soochow University (Suzhou, China) in October 2013, and there he established the Laboratory for Clothing Physiology and Ergonomics (LCPE), a multidisciplinary research group for the study of the thermal interaction of the human body-clothing-environment system. To date, he has authored or coauthored more than 200 journal publications, conference papers/presentations, technical reports, books/chapters, and patents. His published work has been cited more than 1,000 times, and this gave him an h-index of 19 (Google Scholar, as of April 2018). In addition, he serves as an editorial member for several journals including *Journal of Thermal Biology* (a JCR-Q1 journal). He is also a founding member of the Asian Society of Protective Clothing (ASPC).

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1

Textiles for Firefighting Protective Clothing

Abu Shaid, Lijing Wang, and Rajiv Padhye

1.1 Introduction

Firefighters' protective clothing (FPC) is the part of the safety outfit of firefighters on duty that protects them from dangers associated with heat, flame, hot or toxic liquid contact, abrasion, cuts, etc. No clothing material can withstand continuous exposure to flame or can provide comfort for an infinite time in hot environments. Hence, fire protective clothing does not necessarily mean the fabric is completely resistant to fire and heat. FPC is designed to save the firefighters from excessive heat and flash fire conditions by allowing them a time gap for a rescue mission, fighting fire, or withdrawing from direct flame contact. FPC fabrics are required not only to ensure that the clothing does not become a means of secondary ignition and spreading of fire and causing injury, but also to provide a certain degree of comfort from hot and humid situations both externally and internally, while still maintaining acceptable working efficiency through easy and quick movement. Hence, the fiber characteristic, heat source, intensity, time of exposure, and many other variables affect the protection performance. FPC typically consists of an overcoat, trouser, hood, and gloves. Other non-clothing assemblies may include self-contained breathing apparatus (SCBA), hand tools, ropes, etc. In this chapter, fibers and fabrics used in FPC will be primarily discussed, the fire retardant finishing on textiles will be noted, and finally the protection and comfort properties of FPC will be summarized.

1.2 Fibers Used in Firefighters' Protective Clothing

In general, FPC is a multilayer assembly composed of various types of woven and nonwoven fabrics. Conventional fibers such as cotton, wool, and viscose and high-performance fibers such as aramid, polybenzimidazole (PBI®), and polybenzoxazole (PBO) are used in FPC. Each type of fiber has its own advantages and disadvantages. One fiber may be effective in protecting from heat but may not be comfortable enough to wear; one may be comfortable but can be very expensive. In protective concern, one particular fiber may possess high tensile strength but may lack heat resistance, while another may have exceptionally good heat resistance but may lack tensile strength. From comfort perspective, one fiber may have good feel with smooth and soft handle but may lack moisture absorption, while another may have good moisture absorption properties but may lack of handle. The choice of fiber or fiber blend for FPC is challenging and requires deep understanding on the requirement of fiber properties. A balance between protection and comfort properties is essential for FPC.

Desired performance for FPC often needs to compromise with cost, availability, and processing limitation. To simplify the discussion, the fiber choice for FPC can be summarized in two general groups.

Group A: High-performance fibers that are inherently flame-retardant (FR), such as polyamide (Kevlar®, Nomex®), polyimide fiber (P84®), PBI®, polybenzoxazole (Zylon®), modacrylic or oxidized acrylic (semicarbon), etc. Flame retardancy is inhabited into their structure at their synthesis stage (Holmes, 2000a), and these fibers have a limited oxygen index (LOI) value above 21% as shown in Figure 1.1 and Table 1.1. LOI indicates the percentage of oxygen that has to be present to support combustion after ignition (ASTM D2863-00—minimum oxygen concentration to support candle-like combustion of a polymer).

Group B: Conventional fibers from both natural and synthetic origin that are not normally FR, but modified to do so after their natural production or synthesis, such as FR cotton, FR viscose, FR wool, etc.

According to Horrocks (2016), the conventional fibers treated with FR are usable up to 100°C continuous use, and those high-performance fibers are suitable for continuous use above 150°C. In this way, Group B fibers are more useful in flame-resistant bedding, upholstery, curtains, etc. other than firefighting application. Hence, some key high-performance inherently FR fibers from Group A are discussed here, and only polyester and FR viscose are noted in this chapter.

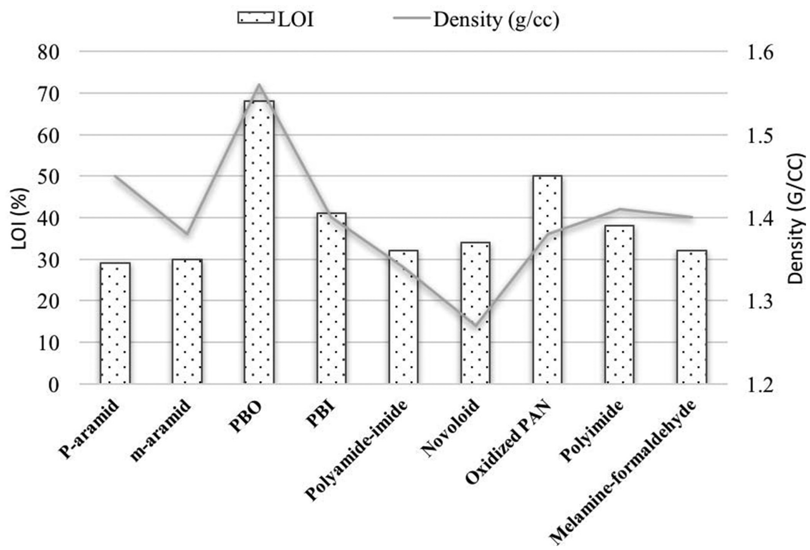

Figure 1.1

The limiting oxygen index and density of some prospective fibers for FPC.

1.2.1 Aromatic Polyamide

Aromatic polyamides (Figure 1.2) or aramid fibers are the most common fibers used in firefighters' garments. In aramid fibers, at least 85% of the amide linkages are attached directly to two aromatic rings; this distinguishes them from conventional polyamide fibers like nylon, which contains mostly aliphatic or cycloaliphatic units (Yang, 1993).

Among both types of aramid in Figure 1.2, poly-*p*-phenylene terephthalamide or *p*-aramid fiber is a liquid crystal polymer that is spun as a bundle of oriented polymer chain (crystal) and does not require any additional drawing step after immersion through the spinneret.

Liquid crystal polymer (LCP) fibers are either lyotropic or thermotropic. Lyotropic LCP, such as aromatic polyamide (*p*-aramid), have a high melting point that is close to their decomposition temperature. Hence, these polymers are not melt-spun but wet-spun. On the other hand, thermotropic LCP fibers such as aromatic polyester (Vectran®) are spun in the melt spinning process as these polymers melt at high temperature. Vectran will melt before decomposition when it is heated while *p*-aramid will produce char. The molten polymer will cause extra hazards while the char will provide an extra layer of heat and flame protection. Hence, Vectran is not used in FPC, but *p*-aramid is used. The prime attractions for the *p*-aramid fiber are its very high tensile strength, tear resistance, flame retardancy (see Table 1.1), and high stability to chemicals. *P*-aramid fiber is self-extinguishing and also possesses low electric conductivity. At the same time, a drawback of aromatic polyamide is their poor light stability together with loss of tear resistance (Lempa, 2009). *P*-aramid is available under different trade names from different manufacturers worldwide such as the most versatile Kevlar® fiber by DuPont, Technora® by Teijin, and Twaron® by Acordis.

Table 1.1 Summary of Some Prospective Fibers Which Have Favorable Characteristic to be Used in FPC in One or More Aspect

Fiber	T_m, °C (Melt)	T_p, °C (Pyrolysis)	T_i, °C (Ignition)	Continuous Operating Temp	LOI vol%	Density, g/cm³	Moisture Regain,%	Strength (cN/dtex)	Price* (US$/kg)
m-Aramid (Nomex)	375–430	425	> 500	200	29–30	1.38	4.5	4.8	20
p-Aramid (Kevlar)	560	> 590	> 550	190	29	1.45	4.5	20.3	25
Polyimide (P84®)	* * (315, Tg)	**	**	260	38	1.41	3	3.5–3.8	**
Polyamide-imide (kermel®)	* * (> 315, Tg)		**	200	30–32	1.34	~4	2.45–5.88	**
PBO (Zylon®)	650 , decompose	**	**	310	68	1.56	0.6–2	37	130
PBI	* *	> 500	**	250	41	1.43	15	2.4	180
Polytetrafluoroethylene (PTFE)	> 327	400	** (560, combustion)	275	95	2.2	0	1.4	50
Melamine fiber (Basofil®)	**	**	**	190–200	30–32	1.4	5	2–4	16
Polyester	255–260	420–447	480		17–20	1.38	0.4	8	3

(*Continued*)

Table 1.1 (Continued) Summary of Some Prospective Fibers Which Have Favorable Characteristic to be Used in FPC in One or More Aspect

Fiber	T_m, °C (Melt)	T_p, °C (Pyrolysis)	T_i, °C (Ignition)	Continuous Operating Temp	LOI vol%	Density, g/cm³	Moisture Regain,%	Strength (cN/dtex)	Price* (US$/kg)
Oxidized PAN fiber/ semi-carbon fiber (Panox®)	**	**	**	200	55	1.38	10	1.6–1.7	10
Novoloid/cured phenol-aldehyde fiber (Kynol®)	* *		> 2500	200	30–35	1.27	6	1.2–1.6	15–18
PVC	> 180	> 180	450	**	37–39	1.4	0	2.4–2.7	**
Cotton	**	350	350	**	16–18.4	1.52	7–8	1.5–4	**
Wool	**	245	570–600	**	25	1.31	14–18	1.1–1.4	**

Source: Bajaj, P., & Sengupta, A. K., 1992, Protective Clothing. *Textile Progress*, 22(2–4), 1–110; Bourbigot, S., & Flambard, X., 2002, *Fire and Materials*, 26(4–5), 155–168; Reprinted from R. A. B. L. Deopura, M. Joshi, & B. Gupta (eds.), *Polyesters and Polyamides*, Butola, B. S., Advances in Functional Finishes for Polyester and Polyamide-Based Textiles, pp. 306–325, Copyright 2008, with permission from Elsevier; Evonik, 2017b, P84® Fibre Characteristics. Retrieved 16 Feb. 2017 from http://www.p84.com/sites/lists/RE/DocumentsHP/p84-fibre-technical-brochure.pdf; Hearle, J. W., 2001, High-Performance Fibres: Elsevier; Horrocks, A., 2005, Thermal (Heat and Fire) Protection. *Textiles for protection*. Woodhead Publ. Ltd, Cambridge, 398–440; Horrocks, A., 2016, Technical Fibres for Heat and Flame Protection. *Handbook of Technical Textiles: Technical Textile Applications*, 2, 243; Kermel, 2013, Kermel®: High Performance Fibre. Retrieved 20 Feb. 2017 from http://www.kermel.com/fr/Production-of-High-Tech-non-flammables-Fibres-640.html; Kynol, 2012, Kynol Novoloid Fibers. Retrieved 20 Feb. 2017 from http://www.kynol.de/products.html; SGL Group, 2017, Panox® Thermally Stabilized Textile Fiber. Retrieved 20 Feb. 2017 from http://www.sglgroup.com/cms/international/products/product-groups/cf/oxidized-fiber/index.html?__locale=en; Swicofil, 2015, Polyamide-Imide PAI. Retrieved 20 Feb. 2017 from http://www.swicofil.com/products/223polyamideimide.html; Toyobo, 2015, The Strongest Fiber with Amazing Flame Resistance. Retrieved 14 Feb. 2017 from http://www.toyobo-global.com/seihin/kc/pbo/zylon_features.html.

* Price shown is for comparison only which is derived from ref (Hearle, 2001). Price does not reflect current market price.

** Not applicable or data not available.

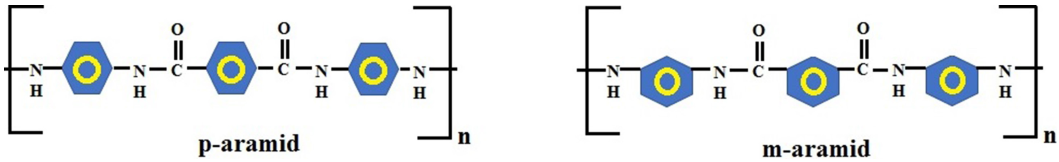

Figure 1.2

Chemical structure of aramid fiber.

Poly-*m*-phenylene isophthalamide or *m*-aramid shown in Figure 1.2 is another aromatic polyamide (Cook, 1980; Gohl, 1985; Moncrieff, 1975) commonly available in FPC. *M*-aramid fiber is also available under various trade names such as Nomex® and Corex®. *M*-aramid fibers are not as strong as the *p*-aramid but have superior heat resistance properties. This particular characteristic makes them a prime choice for the thermal liner in FPC.

1.2.2 Polybenzimidazole Fiber (PBI and PBI Gold)

Polybenzimidazole or PBI is nonflammable in air under normal conditions (Jackson, 1978). Though it is a costly fiber, it offers improved thermal protection and flame resistance property. The Federal Trade Commission (FTC) defined PBI as a manufactured fiber in which the fiber-forming substance is a long-chain aromatic polymer having recurring imidazole groups as an integral part of the polymer chain (Gooch, 2011). Imidazole derivatives are well known for their stability to high temperature (645°C) and resistance to the most drastic treatment with acids and bases (Hofmann, 1953). PBI is the condensation polymer from imidazole, which contains the repeating cores of benzimidazole (Vogel & Marvel, 1961) and also exhibits extraordinary heat stability. It is polymerized from the condensation reaction of tetra-aminobiphenyl and diphenyl isophthalate (Hagborg et al., 1968; Jackson, 1978). Though the PBI polymer development was started around the mid-1950s (Jackson, 1978), they became widely recognized in 1961 when Vogel and Marvel (1961) developed PBI with wholly aromatic structure, as shown in Figure 1.3. Due to the exceptional thermal stability of PBI, NASA started to use PBI in their space suits to protect the astronauts from fire in 1969. PBI was introduced for FPC in the 1980s to replace the old-fashioned Kevlar-leather-Nomex turnout gear and PBI continues its success for FPC. Many of the firefighters who died in the 9/11 terrorist attack were identified only by their PBI turnout gear (Pearson, 2007).

PBI can be processed in conventional textile machinery and can be blended with other similar fibers. Hence, to optimize the cost in relation to the desired

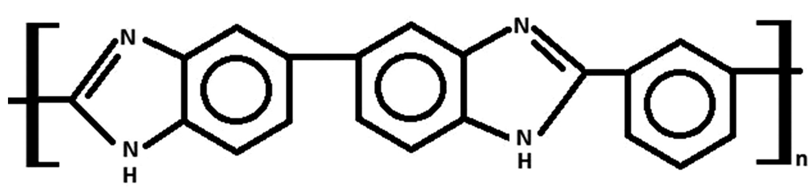

Figure 1.3

PBI structure.

performance, PBI is often blended with aramid. Researchers found that a 60/40 blend of aramid (Kevlar) and PBI can offer optimal overall fabric performance (Bajaj & Sengupta, 1992; Barker & Coletta, 1986). This blend ratio became well known by the name of PBI Gold. As a single fiber, PBI is much weaker than Kevlar as shown in Table 1.1. However, PBI Gold is reported for its high tear strength and high heat resistance in the FIRES (Firefighters Integrated Response Equipment System) project report by the International Association of Firefighters (IAFF) (Gore, 2010).

1.2.3 Polyimides

P84® is an inherently nonflammable, non-melting polyimide fiber manufactured by Evonik Fibers (Evonik, 2017a). Its structure is shown in Figure 1.4. The LOI of P84 is 38% and glass transition temperature (Tg) is 315°C, which are much better than aramids (Kevlar, Nomex, and PBI), as seen in Table 1.1. The fiber starts to carbonize above 370°C and is suitable for continuous use at temperature up to 260°C. P84 has suitable feel, comfort, and performance properties to be used on their own or in blend with FR viscose for protective clothing (Bajaj & Sengupta, 1992).

1.2.4 Polyamide-imide

Kermel® is a polyamide-imide fiber under the classification of meta-aramid. Its structure is shown in Figure 1.5. In France, Kermel is especially used for FPC (Bajaj & Sengupta, 1992). The fiber can withstand very high temperature up to 1000°C for a short time exposure such as flash fire condition. The fiber itself does not melt or decompose, but it slowly chars when exposed to very high temperature. Hence it is suitable as the outer layer of firefighter protective clothing. Kermel fiber is soft to handle due to its smooth circular surface and can be solution dyed. Kermel can be found in turnout gear as a blend with other high-performance fiber.

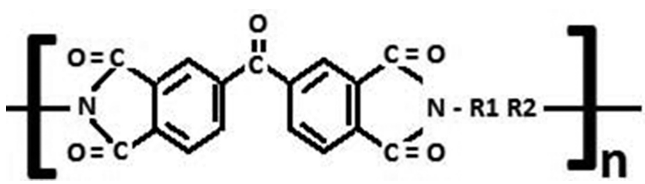

Figure 1.4

P84® chemical structure.

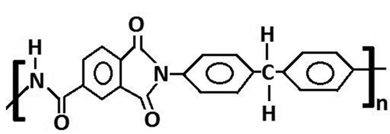

Figure 1.5

Kermel fiber structure.

1.2.5 PBO (Polybenzoxazole)

Zylon is another liquid-crystalline PBO (poly(p-phenylene-2,6-benzobisoxazole)) fiber, which is around 1.6 times stronger than Kevlar and 10 times stronger than PBI fiber. Its decomposition temperature is 650°C and LOI is 68% (Toyobo, 2015). Thus, the flame resistance and heat resistance of Zylon are significantly higher than those of PBI and aramid. However, the PBO fiber is not only heavier than aramid and PBI but also more costly. Hence, PBO often blends with aramid or PBI to provide a balance performance in FPC.

1.2.6 Novoloid (Cured phenol-aldehyde) Fibers

Novoloid is a highly flame-resistant fiber with soft handle and comparatively better moisture regain. Kynol® is a commercially available Novoloid fiber manufactured by GunEi Chemical, Japan (GCI, 2017). The fiber contains at least 85% crosslinked novolak, and is infusible and insoluble. In flame exposure, Kynol does not melt but gradually chars to complete carbonization. A Kynol fabric of 290 g/m^2 (gsm) can withstand 2500°C for 12 without breakthrough (Kynol, 2012), while the practical temperature to use is only around 150°C for long-term application. However, though Kynol has soft handle and comparatively higher moisture regain, it is comparatively a weak fiber with low tenacity. It can be blended with other high-performance fibers such as Nomex or FR viscose for improved fabric physical properties (Bajaj & Sengupta, 1992). Thus, novoloid fibers may not be usable as an outer layer, but they are ideal candidates for nonwoven felt structure for batting material in the thermal liner of FPC.

1.2.7 Oxidized PAN

The partial carbonization of polyacrylonitrile fiber results in oxidized PAN or semi-carbon fiber. Unlike carbon fiber, semi-carbon fiber retains acceptable textile properties after high-temperature oxidation. Semi-carbon fibers were commercially available from different manufacturers such as Celanese, Courtaulds, Asahi, SGL, and so on, but many of them are now obsolete. Panox® from SGL is an example of oxidized PAN fiber with 62% carbon content, which is produced by thermal stabilization of PAN in 300°C (SGL Group, 2017). The fiber does not burn, melt, or soften to drip. Panotex fabric made from Panox can withstand direct flame contact temperature in excess of 1000°C and is resistive to most common bases and acids (Bajaj & Sengupta, 1992). However, it has low strength. Hence, it is used in thermal liners of FPC as a blend with other fibers.

1.2.8 Melamine Fiber

BASF developed a comparatively cheaper and inherently flame-retardant melamine fiber called Basofil® in the 1980s (Murugesan & Gowda, 2012). It is a melamine-based staple fiber with high-temperature resistance properties. The main drawback of this fiber is its low strength. Hence, it can be blended with other high-performance fibers such as aramid to improve the strength and abrasion resistance (Horrocks, 2016). The prospect of its use in FPC is in the form of felt or nonwoven as a thermal barrier material.

1.2.9 Inorganic and Ceramic Fiber

Glass and ceramic fibers may be used in protective apparel primarily as nonwoven felt by blending with other fibers. Detailed properties of these fibers are extensively discussed in research literature (Bourbigot & Flambard, 2002; Moncrieff, 1975).

1.2.10 Conventional Fibers with Added Flame Retardancy

Some conventional textile fibers are used in FPC in blend or in rare case as a single internal layer. FR finishing of cellulose fiber is discussed in Section 1.4. In this section, FR polyester and viscose will be discussed in brief. FR additives are added during their synthesis process instead of FR chemical finishing.

a. **Flame-Retardant Polyester**
   The linear polyester is normally highly flammable as it produces a variety of volatile and flammable products upon heating. Among the varieties of polyester fibers, poly(ethylene terephthalate) (PET) is the most common and widely used polyester fiber. By employing suitable flame-retardant strategies, the thermoplastic polyester can be made resistive to flame. The use of reactive flame-retardant comonomers, such as 2-carboxyethyl(methyl)phosphinic acid or 2-caboxyethyl(phenyl) phosphinic acid, is an effective strategy to achieve long-term fire-retardant effect. HEIM fiber (Fukui et al., 1973) commercialized by Toyobo is an example of FR polyester fiber.
b. **FR Viscose**
   In 1974, researchers from Sandoz Ltd added phosphorus containing flame retardant (dioxaphosphorinane derivatives) in cellulose xanthate dope during the production of viscose rayon to impart flame retardancy (Mauric & Wolf, 1980). More recently, a patent was filed in 2015 and published in January 2017 where it is claimed to produce molded cellulose bodies (fiber, filament, nonwoven) with flame-resistant properties from cellulose and melamine cyanurate solution in an organic solvent (Niemz et al., 2017).

1.3 Membranes Developed for Protective Clothing

Membranes used in FPC are extremely thin (about 10 μm) microporous or hydrophilic polymeric film (Holmes, 2000c). Membranes used in protective clothing can be permeable, semipermeable, selectively permeable, or completely impermeable depending on the specific need of protection. Toxicological agents protective suit used by military is made of an impermeable film that does not allow liquid to pass through, not even water vapor. However, the standard-issue military chemical protection suits allow vapor exchange through a semipermeable absorptive carbon liner where the membrane blocks the liquid passing through but carbon absorbs the chemicals while the vapor passes through the fabric (Schreuder-Gibson et al., 2003). In this section, the membranes suitable for FPC will be discussed under two categories, vapor transportation through pores and vapor transportation by absorption.

1.3.1 Porous Membrane

Porous "perm-selective" membrane (Zhou et al., 2005) is a common element in various protective apparel like firefighters' and chemical protective clothing. It shows selectivity with respect to molecular solubility and diffusion through the polymer structure (Schreuder-Gibson et al., 2003). Water vapor passes through while the organic molecules are blocked. The selective membrane can be made of cellulose acetate, poly(vinyl alcohol), cellulosic cotton, and poly(allylamine) (Schreuder-Gibson et al., 2003). It is used in FPC as a moisture barrier.

Porous Gore-Tex® expanded PTFE (ePTFE) membrane is most widely used as a moisture barrier. Traditional Teflon (PTFE) seal tape for pipe joint breaks when stretched beyond a certain limit. However, a sudden hot stretch can allow it to expand about 800%, which creates thousands of tiny pores that allow the moisture vapor to pass through. In fact, Gore-Tex membrane contains more than 9 billion pores per square inch (Gore, 2017). It acts as a barrier to liquid moisture (water droplet) but allows water vapor (sweat) to escape to the environment. In 1969, Gore realized the potential of the pores and patented ePTFE membrane/film. Gore-Tex membrane acts as the moisture management medium. In FPC, various Gore-Tex moisture barrier layer fabrics are used such as CROSSTECH®, GORE® RT7100, GORE® PARALLON™, etc.

Alternatives of commonly used Gore-Tex membrane are also slowly emerging. Apart from ePTFE membrane, microporous membranes from PU (polyurethane) are also manufactured and marketed for FPC (Mukhopadhyay & Midha, 2016). PVDF (polyvinylidene fluoride) membrane is also available from other manufacturers for the same purpose (Holmes, 2000c) of Gore-Tex membrane. Nanofiber web or foam is another alternative to ePTFE membrane. Casting of an electrospun nanofiber layer on base fabric is another mechanism of pore formation and imparting breathability in protective clothing (Raza et al., 2014). Bagherzadeh et al. (2012) sandwiched electrospun nanofiber web between woven fabric layers to prepare a breathable textile barrier and compared its performance with Gore-Tex membrane. Serbezeanu et al. (2015) electrospun polyimide membranes on Kevlar base fabric to prepare a barrier material. Open cell foam is another porous vapor transmission technique that is used in protective clothing (Holmes, 2000a).

1.3.2 Nonporous Membrane

Unlike semipermeable and perm-selective membranes, impermeable types of membranes do not contain any pores. These can be polyester or polyurethane film, chemically modified to gain hydrophilic nature through the amorphous region of their polymeric system (Holmes, 2000c). Thus, the solid film prevents the liquid drops whereas the water vapor is attracted by the hydrophilic group of the chain modifying agent. Driven by the vapor density and heat, water vapor diffuses in the polymer system and finally escapes to the environment from the opposite surface.

1.3.3 Combined Porous–Nonporous Membrane

This is a combination of microporous and hydrophilic membrane. In this case, a nonporous hydrophilic coating is applied to a microporous membrane. In traditional microporous membrane, pinholes or oversized pores may cause water leakage. On the other hand, the pores can also be blocked by contamination (e.g., body oil, dirt, or other foreign materials). However, in this type of combined membrane, the nonporous hydrophilic layer seals the microporous membrane and offers better performance.

1.4 Fabrics and Nonwovens Used in FPC

Firefighters' protective gear is a system or assembly combining both textiles and nontextiles to serve the sole purpose of keeping firefighters safe and functional in various hazardous situations. The turnout coat worn by the firefighters has traditionally been a multilayer structure containing an outer shell, moisture barrier, and thermal barrier. The outer layer and the face cloth of the thermal barrier of FPC are normally plain or twill-woven fabric, whereas the moisture barrier and batting of the thermal barrier are nonwoven. In this section, the textile component of FPC (turnout coat and trouser) will be discussed. The following sections briefly highlight these three layers of FPC.

1.4.1 Outer Shell Fabric

The outer shell is the first line of defense for firefighters. The protection required has various aspects and no single fabric can meet all of those. The outer shell fabric should protect the firefighters from fire in flash-fire conditions or when entering a burning building. It needs to have sufficient tensile strength with acceptable abrasion and cut resistance to support crawling or climbing in rescue missions. FPC also needs to be lighter, flexible, and breathable to avoid heat stress and hindrance in movement. Hence, the fiber choice for outer layer is important and needs to consider price, performance, and comfort. The fiber for the outer layer is traditionally selected from any of the high-performance inherently flame-retardant fiber from Group A as discussed in Section 1.2. As approximately 21% oxygen is present in air, any fiber with a LOI value over 21% will not support combustion in air. Thus, the higher the LOI value is, the lower the flammability risk will be. In general, a fabric to be defined as flame retardant should have a minimum LOI value of 26–28% (Horrocks, 2016). Aramid, PBI, and their blends are commonly found in the outer layer fabric of current FPC due to their price and favorable properties. However, due to the emergence of new technologies and novelty fibers, manufacturers of FPC are continuously developing favorable blends with various fiber alternatives to bring optimum balance in price, comfort, and protection (Figure 1.6).

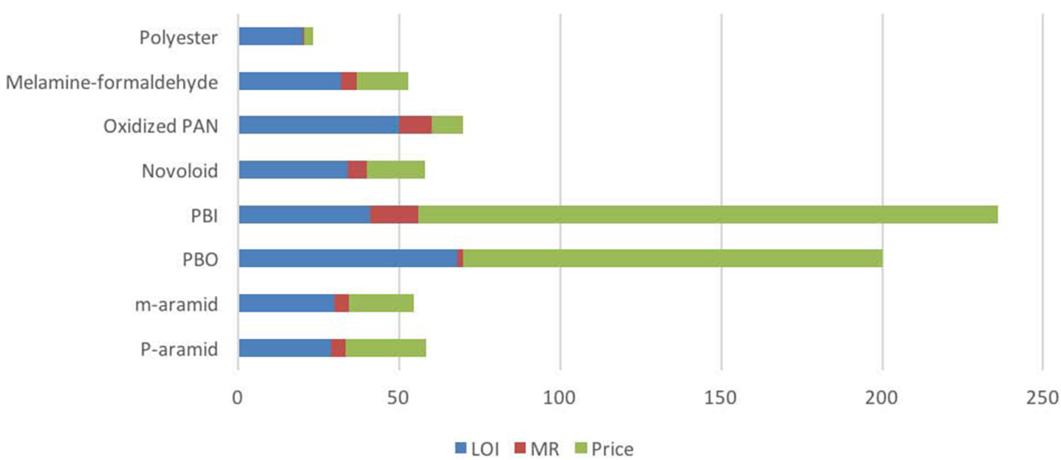

Figure 1.6

Price-Peace-Protection trilogy in terms of fire protection and moisture absorption.

It is a reality that no single fiber can meet all the requirements as an outer layer fiber. As an example, the widely used *p*-aramid is famous for its strength and abrasion resistance, but it suffers from degradation and strength loss when exposed to sunlight. *M*-aramid and PBI are comparatively more stable to ultraviolet degradation and have better heat resistance, but they lack strength. One fiber may have a high LOI value but lower melting temperature (such as PVC), whereas some non-melting fiber (such as Novoloid, wool) may have a comparatively lower LOI value.

The selection of a suitable fiber type and fabric structure is another important consideration. McQuerry et al. (2015) collected more than 250 FPC from various fire departments and evaluated their performance on ageing. Diversified material choice was seen in this study. The outer shell fabrics included Nomex, Kevlar, and PBI. Moisture barriers included Aquatech, Crosstech, Goretex, PTFE membranes, and RT71000. The thermal liners were composed of TenCate Caldura SL Quilt, aramid fibers, and E-89. Lee and Barker (1987) evaluated the thermal protective performance of 21 heat-resistant fabrics of knit, woven, and nonwoven structure. The fabrics tested were either aramid or PBI, and PBI blends with aramid or FR rayon. The woven fabrics were on twill, sateen, or plain structure with fabric weight ranging from 139 to 295 gsm. Fabric weight of tested knit structure ranged from 153 to 298 gsm and felt structure ranged from 180 to 295 gsm. Wang et al. (2011) evaluated the moisture transfer performance of several FPC assemblies that include nine outer layer fabrics composed of blends of aramid, PBI, Kermel, Tanlon, and carbon Antistatic. The fabric weight ranges from 150 to 260 gsm. Krasny et al. (1982) evaluated eight commonly used outer shell fabrics composed of aramid, novoloid, cotton, and their blends where the fabric weight ranges from 205 to 440 gsm. Hence, it is worthwhile to consider fabric construction to choose a suitable outer layer fabric from the wide range of commercial products. Table 1.2 presents some examples of commercial outer shell fabric from the recent market trend of fiber blend.

FPC is mostly constructed on basic weave structures. These include mainly plain or twill construction and their special derivatives such as ripstop construction, comfort twill, etc. Satin weave is not a practical option for FPC.

Plain weave is the simplest, shortest, and most important woven fabric construction produced by alternative lifting and lowering of one warp yarn across one weft yarn. It has the maximum amount of interlacing possible in a woven fabric. Plain weave produces a tight cloth with firm structure, which is stronger than any other weave structure (Redmore, 2011; Wilson, 2001). Hence, at least 90% of the two-dimensional woven technical fabrics are constructed on plain weave (Sondhelm, 2000).

Twill weave is another basic weave structure where diagonal rib lines become visible on the fabric surface. Rib lines usually run from the lower left to the upper right of the fabric where each end floats over or under at least two consecutive picks (Rouette & Schwager, 2001). Thus, the twill weave has more open construction with longer floats and fewer intersections.

Derived weave structure is derived from the three basic types (plain, twill, and satin) or their combination. For example, leno, repp, and panama are derived from plain weave; honeycomb and herringbone are derived from twill; and crepe, shadow repp, etc. are derived from satin (Rouette & Schwager, 2001).

Table 1.2 Outer-Shell Fabrics from Various Manufacturers

Trade Name	Manufacturer	Description	Structure
Advance™	Southern Mills, Inc, doing business as TenCate Protective Fabrics USA Inc	60/40 blend of KEVLAR® and NOMEX® used for outer shell fabric, piece dyed	Ripstop
Nomex® IIIA	DuPont	93/5/2 Nomex-Kevlar-Carbon	Plain
Indura®	Westex by Millimen & Co	100% FR cotton	Rugged Twill
Fusion™	Safety components	60/40 or 50/50 Kevlar-Nomex blend	Ripstop
Armor AP™	Safety components	80/20 or 60/40 Nomex-Kevlar blend	Twill
PBI Max™	Safety components	70/30 PBI-Kevlar blend	Comfort-Twill
PBI Matrix®	Safety components	60/40 Kevlar®-PBI Gold Plus®	Plain
Armor 7.0 ™	Safety components	75/25 or 50/50 DuPont Kevlar-Nomex	Comfort-Twill
Millenia™	Southern Mills, Inc/TenCate Protective Fabrics USA Inc	60/40 Tejin Twaron or Technora-Zylon PBO	Ripstop
Advance Ultra	Southern Mills, Inc/TenCate Protective Fabrics USA Inc	60/20/20 Kevlar-Nomex - Zylon PBO	Ripstop
Omni Vantage™	Norfab corporation	40/30/30 Kevlar-Basofil-Nomex	Ripstop
Gemini™ XT	Southern Mills, Inc/TenCate Protective Fabrics USA Inc	55/37/8 Kevlar-PBI-Vectran or Technora	Plain
Pioneer™	Southern Mills, Inc/TenCate Protective Fabrics USA Inc	60/40 or 50/50 Nomex/Kevlar	Twill
Ultra®	Southern Mills, Inc/TenCate Protective Fabrics USA Inc	Kevlar/Nomex/PBO	Ripstop
Kombat™ Flex	Southern Mills, Inc/TenCate Protective Fabrics USA Inc	PBI/Kevlar	Twill
Dual Mirror®	Gentex corporation	Aluminized PBI/Kevlar	Ripstop
Tecasafe® Plus	Southern Mills, Inc/TenCate Protective Fabrics USA Inc	Modacrylic/cellulose/aramid	Twill
Defender M®	Southern Mills, Inc/TenCate Protective Fabrics USA Inc	Lenzing FR® Rayon-para aramid-Nylon	Ripstop
Brigade™	Southern Mills, Inc/TenCate Protective Fabrics USA Inc	Nomex®	Plain

Source: Component, S., 2017, Outer Shells. Retrieved 22 Feb. 2017 from http://www.safetycomponents.com/Fire/Outershells/; FireDex, 2017. Fxr Custom Turnouts-Materials. Retrieved 22 Feb. 2017 from http://www.firedex.com/product/fxr-custom-turnouts/; Honeywell, 2013, Honeywell First Responder Products. Retrieved 22 Feb. 2017 from http://www.honeywellfirstresponder.com/~/media/epresence/firstresponder/literature/pdf/selector%20guides/fabric%20selector.ashx?la=en; Topps, 2016, Flame-Resistant Fabric Information. Retrieved 22 Feb. 2017 from http://www.toppssafetyapparel.com/fabrics.html; Westex, 2017, Westex Fabric Brands. Retrieved 2 March 2017 from http://www.westex.com/fr-fabric-brands/; Veridian, 2017, Materials. Retrieved 22 Feb. 2017 from http://veridian.net/materials.php.

Ripstop weave is a widely used woven fabric structure in technical textile industry. It is designed to stop the ripping. Extra high strength yarn is weaved in regular interval within the normal base fabric to provide resistance to spreading of tear. The definition of ripstop weave is given as "very fine woven fabric, often nylon, with coarse, strong warp and filling yarns spaced at intervals so that tears will not spread. The same effect can be achieved by weaving two or three of the fine yarns together at intervals" (Wingate, 1979, p. 513). It is suitable for technical textiles that required resistance to tear. In 2005, Du Pont patented weave fabric structure specially designed for FPC with ripstop yarn component where the ripstop yarn has at least 20% more tensile strength than the body yarn (Zhu & Young, 2005). Nowadays, many manufacturers use ripstop construction for fabric intended as an outer layer fabric of FPC.

Miscellaneous: Manufacturers of technical textile fabrics developed innovative weave construction based on any of those basic structures for fulfilling specific requirements. *Rain drop* and *Comfort twill* are recent examples of such development. *Comfort twill* is based on patented Filament twill™ technology by *Safety Component*. This weave structure can be found in the outer layer fabrics such as PBI Max™, Armor AP™, or in thermal liner Glide™. It is claimed that this weave structure from Kevlar filament is over two times stronger than weave structure from Kevlar spun yarn, and also the fabric is more flexible, lightweight, and comfortable (Safety Components, 2017). Another such special construction is "Channeling raindrop" weave, which is being used in the Prism™ thermal liner. It is woven in a technical pattern, which positions a higher ratio of viscose. Since viscose has excellent wicking capability, such concentrated placement inside raindrop pattern absorbs and allows moisture to be channelled away from the wearer for enhanced comfort. Many other special weave structures are available for technical textiles, but those are not discussed here. Here the two special weave constructions highlight the idea of continuous weave modification trend in today's competitive market culture to meet specific requirements.

1.4.2 Moisture Barrier

The purpose of the moisture barrier is to impart breathability in FPC. This barrier layer makes the FPC impermeable to water while it allows the moisture vapor to pass through. In this way, firefighters remain protected against hot water and toxic liquids while the sweat can be vaporized and dissipated to the environment.

Moisture barriers may not be mandatory. In some countries, firefighters like to have their fire suits without a moisture barrier, whereas in other countries it is obligatory (Mäkinen, 2005). Microporous perm-selective membrane, hydrophilic nonporous membrane, or their combination can be used. In most cases, ePTFE membrane is used as a moisture barrier in a bicomponent structure with PU foam that creates an air cushion. Sometimes an additional hydrophilic coating is also applied on top of the ePTFE membrane. Table 1.3 shows some commercially available moisture barriers from various manufacturers.

1.4.3 Thermal Liner Fabric and Nonwoven

Thermal liner of FPC usually contains a nonwoven batting attached to a face cloth, as shown in Figure 1.7. The thermal liner is the most critical component in turnout gear as it has the biggest impact on thermal protection and heat stress reduction. Air is trapped in or between the nonwoven material of the thermal liner, and thus together with the moisture barrier, thermal liner provides 75% of the total thermal protection of a turnout garment (Young, 2010). Figure 1.7 shows a complete fabric assembly in an FPC where a nonwoven batting material is sewed to a facecloth. The face cloth of the thermal liner is conventionally a thin woven fabric from Group A as discussed in Section 1.2.

Table 1.3 Examples of Commercially Available Moisture Barriers

Trade Name	Manufacturer	Composition	Fabric
STEDAIR®3000	Stedfast	Bi-component ePTFE/FR PU	33/67 blend of Kevlar-Nomex® E89™. Nonwoven Spunlace
STEDAIR®4000	Stedfast	Bi-component ePTFE/FR PU	100% Nomex IIIA®. Woven Pajama-check
STEDAIR®Gold	Stedfast	Bi-component ePTFE/FR PU	80/20 blend of Nomex IIIA®-PBI. Woven Pajama-check
CROSSTECH® 3-layer	W.L Gore	Bi-component ePTFE/FR PU	Nomex, Woven Pajama-check
CROSSTECH® black	W.L Gore	Bi-component ePTFE/FR PU	100% Nomex IIIA®. Woven Pajama-check
GORE® RT7100	W.L Gore	Bi-component ePTFE/FR PU	15/85 blend of Kevlar®-Nomex®. Needle punched Nonwoven
Porelle® Membrane	Porelle	Bi-component ePTFE/FR PU or hydrophilic	
Entrant®	Toray Industries	Microporous hydrophobic PU film	

Source: FireDex, 2017, Fxr Custom Turnouts-Materials. Retrieved 22 Feb. 2017 from http://www.firedex.com/product/fxr-custom-turnouts/; Honeywell, 2013, Honeywell First Responder Products. Retrieved 22 Feb. 2017 from http://www.honeywellfirstresponder.com/~/media/epresence/firstresponder/literature/pdf/selector%20guides/fabric%20selector.ashx?la=en; Mukhopadhyay, A., & Midha, V., 2016, Waterproof Breathable Fabrics. *Handbook of Technical Textiles: Technical Textile Applications*, 2, 27; Porelle, 2017, PTFE Membranes- Waterproof, Windproof and Heat Resistant. Retrieved 24 Feb. 2017 from http://www.porellemembranes.co.uk/en/membranes/ptfe-membranes/; Toray, 2017, Toray- All About Sports Fabrics. Retrieved 24 Feb. 2017 from http://www.torayentrant.com/en/about/.

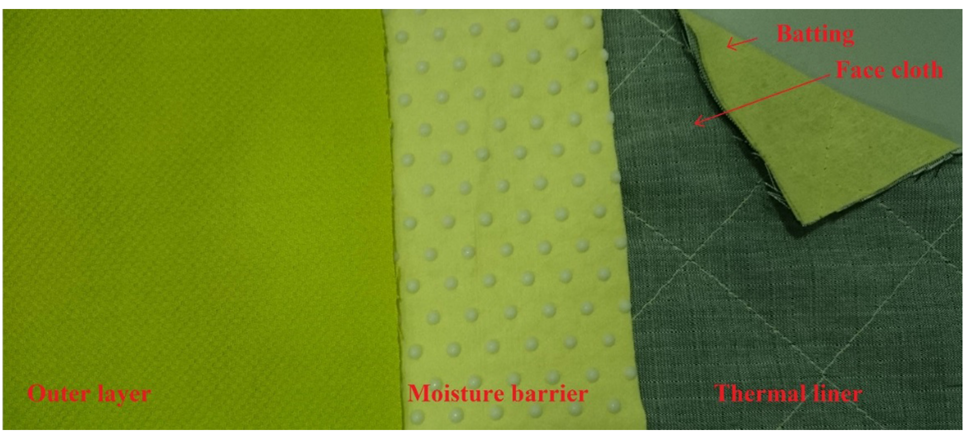

Figure 1.7

Fabric assembly in FPC: from left, Nomex outer layer, STEDAIR moisture barrier, and thermal liner showing nonwoven batting and woven Nomex face cloth.

Nonwoven is a fabric structure built without twisting of the fiber (as in yarn) or interlacing of yarn (as in fabric), resulting in a lofty textile construction unless pressed. Hence, nonwoven textiles can accommodate high volume of air pocket in much lower weight of textile, which can be used as a barrier to heat transmission. In knitted or woven fabrics, fibers are held together by frictional force.

However, in nonwovens, fibers are held together either by frictional force (fiber entanglement) or adhesive system (thermal or chemical bonding). Initially a layer of fiber web (batt) is laid by a suitable method like carding machine, air laying, water laying, spun laying, etc., and then the laid fibers are bonded by means of mechanical entanglement such as needle punching, hydroentanglement, stitch binding, etc. or by means of a thermal/chemical agent (Smith, 2000). Two commonly available nonwoven batting materials of thermal liner are "needle punched" and "spunlace." Table 1.4 shows some examples of commercial thermal liner with their construction, combination, and manufacturer.

Needle punched: Needle punching is a simple stitching of fiber batt with entangled fiber. In this case, a set of needles is punched through the laid fiber batt and then withdrawn. During the needle descending, a strand of fiber is caught by the barbs of the needle and forms loops. On upward withdrawal of the needle, the fiber strand is released from the needle barbs, forming an entangled stitching fiber strand in the laid fiber batt. This is a "down-punched" method. Similarly it can be "up-punch" or a combination of both (a "double-punch").

Spunlace nonwoven: The term "spunlace" was derived from its laying mechanism, not the bonding technique as it was in needle-punched nonwoven. In "spun laying" mechanism, as soon as the filaments are extruded from the spinnerets, they are directly drawn (usually by air) downward to lay into a batt. Then the batt is bonded (typically hydroentanglement) to nonwoven. As the filaments are directly laid to make fabric just after their extrusion from raw material, spunlace nonwoven production is called the shortest possible textile route from polymer to fabric (Smith, 2000). The production process is so fast that a commercially spunlace production line with production speed up to 400 m/min (Andritz, 2016) is available.

Needle punched battings are normally bulkier than spunlace batting. Normally two-layer spunlace batting is used in thermal liner while one layer of needle punched batting does the job in identical condition. However, needle-punched battings usually offer higher thermal protection performance ratings, while spunlace battings offer better total heat loss performance (TenCate, 2016). Needle-punched battings are normally less flexible and less durable than spunlace battings.

1.5 Chemical Finishing

Ignition and burning is a gas phase reaction (Bourbigot et al., 2003) where a mixture of combustible gases with ambient oxygen yields a flame and generates heat (Duquesne & Bourbigot, 2010). The combustion cycle of a solid starts by absorbing heat, which decomposes the solid and creates many smaller components. These smaller molecules diffuse to the surface and escape to the environment, creating a gloomy flame. The pyrolytic decompositions produce carbonaceous char with combustible and noncombustible gases (Duquesne & Bourbigot, 2010). In their way to combustion, combustible gases are oxidized by the oxygen present in the environment and produce more heat, which is absorbed by the remaining parts of the solid, and the combustion cycle continues. Reducing the flammability of textile

Table 1.4 Thermal Barrier Combination in Commercially Available Thermal Liner

Trade Name	Manufacturer	Composition Face Cloth	Weave Face Cloth	Batting
Glide Ice™	Safety Components	60% Kevlar® with 40% Nomex/Lenzing FR®	Twill	2 Layers Nomex spunlace
Prism™	Safety Components	68/21/11 blend of Aramid, FR viscose, and Polyamide	Channeling Raindrop	Nomex/Kevlar needle punch
Bravo™	Safety Components	51/32/17 blend of aramid, FR viscose, and polyamide	*NK	2 layer, 50/50 blend of aramid and FR viscose
XLT-Lite™	Starfield	100% Nomex®	Plain weave	Reprocessed Nomex, Needle punch
Aralite® NP	TenCate Protective Fabric	100% Nomex®	Plain weave	Kevlar®/Nomex®, Needle punch
Aralite® SL3	TenCate Protective Fabric	100% Nomex®	Plain weave	3 Layers Kevlar®/Nomex® E-89™, Spunlace
Defender® M	TenCate Protective Fabric	85-25-10 blend of Lenzing FR®-Twaron®-Nylon	Plain weave	2 Layers Kevlar®/Nomex®, Spunlace
PBI Thermal GUARD™	PBI performance products, Inc	Proprietary PBI Blend	Plain weave	80% Aramid, 20% PBI, Spunlace
Caldura® NPi	TenCate Protective Fabric	61/34/5 blend of Kevlar®-Lenzing FR®-Nylon	Twill	Aramid, Needle punched

(*Continued*)

Table 1.4 (Continued) Thermal Barrier Combination in Commercially Available Thermal Liner

Trade Name	Manufacturer	Composition Face Cloth	Weave Face Cloth	Batting
Caldura® SL2i	TenCate Protective Fabric	61/34/5 blend of Kevlar®-Lenzing FR®-Nylon	Twill	2 Layers Kevlar®/Nomex® E-89™, Spunlace
Glide™ Pure	Safety Component	60/26/14 blend of Kevlar®-Nomex®-Lenzing FR®	Filament Twill	50/50 Kevlar®-Nomex®, Needlepunch
Glide™ 2 layer	Safety Component	60/26/14 blend of Kevlar®-Nomex®-Lenzing FR®	Filament Twill	2 Layers Kevlar®/Nomex® E-89™, Spunlace
Quantum3D® SL2i	TenCate	61/34/5 blend of Kevlar®-Lenzing FR®-Nylon	Twill	2 Layers Kevlar®/Nomex®, Spunlace
Glide ICE™ PBI G2	Safety Component	61/26/14 blend of Kevlar®-Nomex®-Lenzing FR®	Twill	2 Layers 80/20 Aramid-PBI, Spunlace
Q-8™	TenCate Protective Fabric	Meta aramid- FR modacrylic	Woven	Aramid-FR Rayon. Needle punched
Defender M® SL2	TenCate Protective Fabric	Lenzing FR® Rayon-para aramid-Nylon	Twill or plain	2 Layers Kevlar-Nomex. Spunlace
Quantum4™	TenCate Protective Fabric	Aramid, FR Rayon, FR Nylon	Twill	80% Nomex, 20% PBI, Spunlace
Ultraflex®	DuPont	100% Nomex®	Plain weave	Aramid 50/50 Kevlar-Nomex

Source: Component, S., 2017, Outer Shells. Retrieved 22 Feb. 2017 from http://www.safetycomponents.com/Fire/Outershells/; Globe, 2016, Globe Turnout Gear-Materials. Retrieved 5 March 2017 from http://globeturnoutgear.com/education/materials; Honeywell, 2013, Honeywell First Responder Products. Retrieved 22 Feb. 2017 from http://www.honeywellfirstresponder.com/~/media/epresence/firstresponder/literature/pdf/selector%20guides/fabric%20selector.ashx?la=en; TenCate, 2016, Firefighter Protection Lives in TenCate Thermal Barriers. Retrieved 5 March 2017 from http://tencatefrfabrics.com/fire-service/firefighter-thermal-barriers/; Veridian, 2017, Materials. Retrieved 22 Feb. 2017 from http://veridian.net/materials.php.

Note: Nomex® 89™ is a nonwoven fabric produced by DuPont and used in moisture barrier with ePTFE membrane. *NK: Not known.

fibers is basically the interruption of this complex combustion process at one or several points of their combustion cycle, which can be achieved either by chemical incorporation or mechanical addition of fire retardant into the fiber polymer molecules (Joseph & Ebdon, 2008). In general, textile flame can be retarded by using inherently flame-retardant polymer, by chemically modifying the conventional polymer to gain flame retardancy, or by applying flame-retardant chemicals/particles to the material by coating the surface or incorporating them into the structure (Bourbigot & Duquesne, 2007; Duquesne & Bourbigot, 2010). High-performance flame-retardant fibers and modified flame-retardant fibers are discussed in Section 1.2. In this section, the principle of flame retardancy is briefly discussed, and then the mode of chemical flame-retardant finishing is noted.

1.5.1 Three Simplified Principles of Flame Retardancy

To retard the flame, it is necessary to interfere with the combustion process in one or several stages. The reactions interfering with the combustion process may act either in condensed or gas phase. Breakdown of polymer to withdraw from flame and formation of char or ceramic-like structure on material surface is the type of retarding effect that takes place in the condensed phase. In the gas phase, the retarders interfere the exothermic reactions and cool down the system to reduce the emission of pyrolysis gases (Duquesne & Bourbigot, 2010). The flame retardancy action can be simplified in three basic principles: (1) the halogen system that interferes in oxidation reaction, (2) the char formation by phosphorus and boron compounds where the retarding action is done by forming an incombustible char on the material surface, and (3) in the endothermic principle where the decomposition of additives absorbs heat to cool down the system and delay the reaching of ignition temperature. Chlorinated paraffins or polybrominated diphenyl ethers are halogenated compounds that liberate halogen atoms that interfere with the oxidation process (Joseph & Ebdon, 2008) and retard the flame. Phosphorus and boric acid based additives work on intumescence phenomenon principle (Bourbigot et al., 2004). They create a low thermal conductive shield that protects the material by reducing the degradation rate and thus lowering the emission of pyrolysis gases (Duquesne & Bourbigot, 2010). For example, phosphorus additives form an incombustible char that protects the residual polymer under char from flame (Joseph & Ebdon, 2008). Di- or tri-alkyl phosphates, tri-aryl phosphates, etc. (Duquesne & Bourbigot, 2010) are typical examples of organic phosphates. A high amount of char means less combustible product for the flame to continue. On the other hand, the retardant effect of hydroxide is threefold. It goes through endothermic decomposition that cools the material, forms inert gases that dilute the flammable gases mixture, and also forms an oxide protective barrier (Duquesne & Bourbigot, 2010). The use of aluminium trihydroxide is an example of such type of retardancy.

1.5.2 The Mode of Flame Retardant Finishing of Textiles

Flame retardant finish can be durable, semidurable, and nondurable. A flame-retardant finish will be durable if the retardant can trap itself in the polymeric structure of the fiber by creating a chemical bond or can be on the substrate surface by durable coating (Horrocks, 2013). Durable reactive FR can be applied to a natural fiber that contains reactive sites for bonding, whereas surface coating is the most common technique to impart flame-retardant finish for synthetic fiber with little reactivity (Opwis et al., 2011). Nondurable flame-retardant finishing can be applied for disposable textiles such as wall covering, party costumes, or medical gowns (Weil & Levchik, 2008a) and hence less relevant to the current discussion. As the present topic is FPC, only durable and semidurable flame-retardant finishing on cellulosic materials is noted here.

a. **THP Salts or Proban Process:** In this case, a phosphorus-containing material, based on tetrakis(hydroxymethyl)phosphonium (THP) salt (THPC, THPS, THPOH), is reacted with urea to form Proban, which is then padded onto cellulosic fabric (Horrocks, 1986). The bulk of FR finished cellulosic fibers are based on the THP derivatives. It can be applied through a pad–dry–cure–oxidation process (Charles, 1992). After padding and drying, the insoluble polymer formed by the Proban is trapped inside the fiber void and interstices of yarn by mechanical means. The detailed chemistry of the Proban process is discussed by the inventor Robert Cole (1978) and also by Frank et al. (1982). Indura® fabric manufactured by Westex is an example of Proban-treated cotton fabric (blended) that is used in FPC.
b. **Pyrovatex Process:** This is a chemical bonding process where a flame-retardant chemically reacts with cellulose and forms a durable bond. In 1969, Ciba authors (Aenishänslin et al., 1969) demonstrated this process of cross-linking cotton by treating with methylol carbamate agent that formed *in situ* in the fiber. The commercial product is known as Pyrovatex® CP where the main molecule is $(CH_3O)_2P(=O)CH_2CH_2C(=O)NHCH_2OH$ (generally called N-methylol dimethyl phosphonopropionamide) (Weil & Levchik, 2008a). The process uses reactivity of cellulose with N-methylol (Charles, 1992). One disadvantage of Pyrovatex is the slow release of loosely held formaldehyde when stored. Hall, Horrocks, and Roberts (1998) demonstrated the process of lowering formaldehyde release, and together with Ciba, Horrocks (Weil & Levchik, 2008a) developed low formaldehyde grade Pyrovatex. Details on both Proban and Pyrovatex process are commonly available in many other related literatures (Horrocks, 1986; Weil & Levchik, 2008b; Yang, 2013).
c. **Semidurable FR Finish of Cellulose:** Semidurable finish can survive water soaking but generally cannot withstand alkaline laundering conditions. One approach is to heat cellulose with phosphoric acid or ammonium phosphates to produce cellulose phosphate. However, as the phosphorylation occurs in glucose unit, it degrades the polymer chain and causes yellowing (Weil & Levchik, 2008a). Use of urea or dicyandiamide as a coreactant along with phosphoric acid or ammonium salt minimizes the damage. Today dicyandiamide salt of phosphoric acid is commercially available for FR finish of cellulose. Again, the use of organic phosphonic acid instead of inorganic phosphate salts/acid and the combination of boric acid and urea has been proven as a more effective semidurable FR finish on cellulose (Dermeik et al., 2006). Flammentin® FMB produced by Thor Specialties and Pyrovatim® PBS produced by Ciba are examples of semi-durable FR finishes.

1.6 Thermal Protective Properties

Protection expected through clothing is multidimensional. For traditional clothing, the expectation is basically social and determines its effectiveness from modesty and cultural value to fashion discerning consumers. However, for protective clothing, values are determined on specific protection performance, limiting cultural or fashion perspective, and even compromising comfort. For firefighting garments, the main concern is protection against heat, which can be experienced from any uncomfortably hot object or direct/indirect contact with flame. The human body can control its internal temperature at a certain level when an external or internal condition changes. Specific central and peripheral nervous systems continuously sense the temperature instability in the body and try to keep a balance through biological action (Li & Wong, 2006). However, under extreme weather conditions, the body needs protection for survival. One of the most important functions of clothing is to protect a wearer against extremes of environmental temperature—either heat or cold (Slater, 1977; Ukponmwan, 1993). The measure of the insulation of a material is its thermal resistance. It is defined as the temperature difference between the two faces divided by the heat flux and has the unit of Km^2W^{-1}. The heat flow can be any form such as conductive, convective, or radiative. Textiles are generally low heat conductive. Hence, convective and radiative heat resistance are primary concerns for designing firefighting protective clothing.

1.7 Thermal Comfort Properties

British Standard BS EN ISO 7730:2005 defines "thermal comfort" as a mental condition of an individual that expresses satisfaction in a thermal condition. Designing protective clothing for firefighters is a challenging task as it requires making a compromise between two crucial but conflicting factors, that is, maximizing thermal protection and minimizing heat stress (Holmér, 1995; Wang et al., 2013). Thermal protection is undoubtedly the primary concern for FPC; however, its effect on metabolic heat stress is also an important consideration (Fanglong et al., 2007). Hence, the FPC needs to be built with a balance of these two factors. The key to thermal comfort is the condition of skin-clothing microclimate, which depends on two vital factors, humidity and temperature. The level of thermal comfort of human body is determined by the heat and moisture balance between body and environment. In brief, this type of comfort can be termed as "thermophysiological wear comfort," which refers to the heat and moisture transport properties of clothing and the way the clothing helps to maintain the heat balance of the body (Song, 2009; Tashkandi et al., 2013). It does not simply depend on one or two key ingredients such as thermal conductivity or insulative behavior of the clothing, but many other minor details, such as environment and wearer's physiomental condition, need to be considered as well. Air velocity affects comfort; the thermal insulation reduces with increased wind velocity as compared with insulation in still air (Ukponmwan, 1993, p. 19). Moisture content of textiles increases the thermal transmissivity (Ukponmwan, 1993, p. 19). Thus, heat, air, and moisture transport properties should be taken into consideration to predict wearer thermal comfort (Barker, 2002; Yoo & Barker, 2005).

1.7.1 Moisture Management

How well a specific fabric type can manage the moisture plays a significant role in wearer comfort. Wearer's perception of moisture comfort sensations and clothing comfort is directly related to absorption of moisture or body sweat by the garment in the garment-skin microclimate, and moisture transportation through and across the fabric where it is evaporated (Benisek et al., 1987; D'Silva et al., 2000; Holme, 2002; Hu et al., 2005). The sweat produced during a firefighting activity should be absorbed from the skin by the surface of the next-to-skin wear and then gradually transferred to the layers further out in the clothing assembly. The use of multiple layers in FPC makes the liquid transfer difficult by reducing the moisture management capability of the garment, resulting in accumulation of sweat on the next-to-skin layer. As a consequence, the wearer suffers increased wet clinginess and thermal discomfort (Houshyar et al., 2017), which may restrict the work time of the firefighter. The fabric does not allow the passage of water vapor, which results in the condensation of water vapor and formation of liquid moisture that is a direct reason of the sensation of discomfort (Srdjak, 2009). Moisture management properties of a clothing are vital in this case. Unlike the simple determination of fabric absorbency and wicking properties, a moisture management test measures the behavior of dynamic liquid transfer in clothing materials. For example, the moisture transportation through FPC is a multidimensional process as fractional amount of moisture can be absorbed in first contact surface, some amount can go through the fabrics, and a small amount can be absorbed in the other surface. For a firefighter, the transfer of external liquid to the skin is not desirable, whereas it is highly expected that the clothing used in FPC should allow the sweat to escape to the environment. These two desirable properties are self-conflicting for any fabric type. How much moisture will be absorbed in the first surface and how much will go to the opposite of the fabric depends on many fabric attributes such as fabric construction, surface finish, etc. Therefore, it is important to analyze the moisture management property of fabrics intended for firefighting gear.

Another important parameter to look for in an FPC fabric is the permeability of moisture, which can be defined in two aspects, transfer of liquid and the permeability index. The former provides an idea of how much protection the fabric type used may offer against harmful liquids from external source, whereas the latter expresses the degree of evaporative cooling (of sweat) of the fabric. The permeability index considers the dry heat resistance of a textile fabric and relates it with the escape of water vapor (sweat evaporation) through the clothing.

1.7.2 Heat Transfer

The temperature between the thermal liner and the firefighter's undergarment can reach from 48°C to 62°C before receiving burn injuries (Rossi, 2003). It has been identified that the pain threshold of human skin is around 44°C (Hardy et al., 1952; Stoll & Greene, 1959). When the skin temperature exceeds this threshold, the absorbed energy determines if and how severe burns will be received (Stoll & Chianta, 1968). The skin receives second-degree burns when skin temperature approaches 55°C (2012). Thus, there is a time gap between starting to feel pain and receiving a second-degree burn. The time between the two points,