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REVIEW

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# Aging of high-performance fibers used in firefighters' protective clothing: State of the knowledge and path forward

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**Abstract**

High-performance fibers developed since the 1960s have a wide range of applications including firefighters' protective clothing. Firefighters' protective clothing made of inherently flame-resistant high-performance fibers offers excellent protection in the new condition. However, these fibers experience aging as any polymer material. The situation is amplified due to the severe conditions associated with the firefighters' activities. And the consequences of a loss in the performance of the protective clothing can be dramatic for the firefighter's safety. This article provides a comprehensively review of the aging behavior of high-performance fibers used in firefighters' protective clothing. Residual performance data have been identified both for used firefighter garments as well as fabric specimens subjected to accelerated aging. Research shows that different aging conditions affect the different fibers to a different degree. The specific conditions in which the aging is applied also affects the outcome in terms of loss in performance. Techniques successfully used to quantify the effect of aging on the performance of fire-resistant fabrics are also briefly mentioned. Finally, the knowledge gained from this analysis of the literature as well as research gaps and further areas of investigation are discussed in this neglected yet critical topic of firefighters' protective clothing aging.

**KEYWORDS**

aging, degradation, firefighting, high-performance fibers, predictive models, protective clothing

## 1 | INTRODUCTION

Protective clothing and personal protective equipment shield the human body from various physical and chemical hazards like puncture, corrosive fluids, and extreme temperatures.[1–3] There are two main categories of protective clothing: primary protective clothing and secondary protective clothing. Primary protective clothing is used when the wearer has the potential of encountering molten substance splashes, extreme heat, and flame. Firefighters' protective gear is an example of primary protective clothing: it is generally put on over the station uniform when responding to a call or performing training. On the other hand, secondary protective clothing is designed to be worn for a more extended period. Specially designed shirts, pants, and coveralls used as firefighters' station uniforms are examples of secondary protective clothing.

Firefighters' protective clothing is one of the major personal protective equipment that keeps firefighters safe and make their job possible.[4,5] Generally, the protective clothing of structural firefighters is a multilayer assembly comprising an outer shell, a moisture barrier and a thermal liner.[6] Figure 1 illustrates these different layers.

According to the standard specification NFPA 1971,[7] the outer shell of firefighters' protective clothing is "the outermost component of an element or item not including trim, hardware, reinforcing material, pockets, wristlet material, accessories, fittings, or suspension systems" (Reference 7, p-16). The fabric that makes the outer shell of firefighters' turnout gear is the most exposed to the hazardous conditions among the three layers.[8] In addition, the outer shell fabric works as a protective barrier for the underlying moisture barrier and thermal liner. As the air entrapped within and between the different layers provides the thermal insulation, a poor outer shell fabric that shrinks will reduce the thermal protection of the assembly.[9]

The outer shell of firefighters' protective clothing is generally made of a woven fabric constructed using a basic weave structure.[8,10] The plain or twill weave structures and some of their derivatives like rip-stop and comfort twill are most often used for the outer shell fabric. In particular, the rip-stop weave structure has recently been favored due to its exceptional tear resistance and increased tensile strength. Figure 2 gives two examples of typical outer shell fabric structures.

As it is the last line of defense for firefighters, the outer shell is designed to resist various types of hazards like extreme heat and flame, toxic chemicals and combustion gases, abrasion and punctures, at least for a short period to allow the firefighter to perform their tasks and retreat to safety.[8] Along with their protective function, outer shell fabrics also need to be flexible and lightweight, so that the protective clothing is not too much of a burden for the firefighters.[4] To provide protection while limiting the negative impact on comfort, various types and blends of high-performance fibers are used to manufacture outer shell fabrics. These heat and inherently flame-resistant high-performance fibers include aramids, polybenzimidazole (PBI), and polybenzoxazole (PBO).[11] Along with inherent flame resistance, some of these fibers also possess high mechanical strength and chemical resistance.

The middle layer of the firefighter bunker suit is the moisture barrier. It acts as a liquid-resistant barrier while offering some level of water vapor transport outside of the garment.[7] Moisture barriers are generally constructed of a membrane laminated to a fabric substrate.[12] The moisture barrier can be laminated to the inside of the outer shell, inserted between the outer shell and the thermal liner or affixed to the outside of the thermal linear

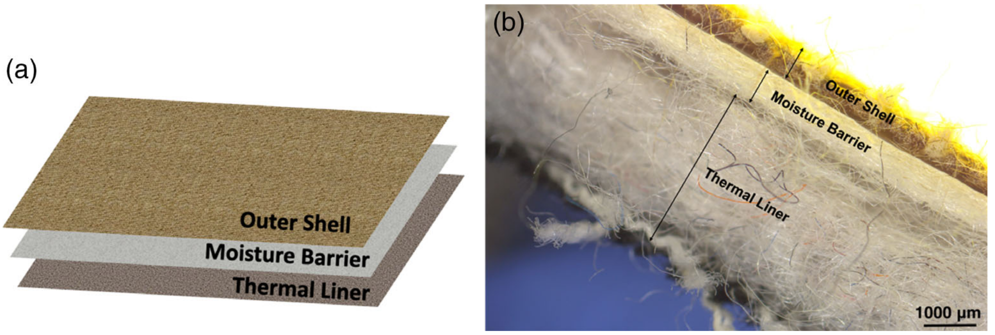


FIGURE 1 Different layers of the firefighters' protective clothing, (a) schematic diagram, (b) optical microscopy image showing the cross-section of the three-layer structure. [Color figure can be viewed at wileyonlinelibrary.com]

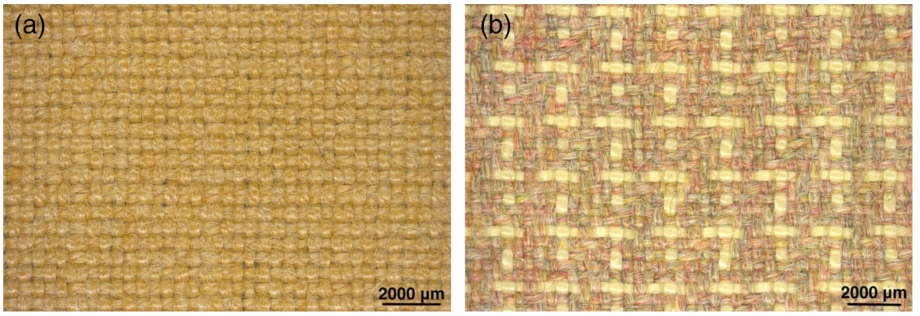


FIGURE 2 Outer shell fabrics used in firefighting clothing ensemble, (a) rip stop weave structure fabric, (b) broken twill weave structure fabric. [Color figure can be viewed at wileyonlinelibrary.com]

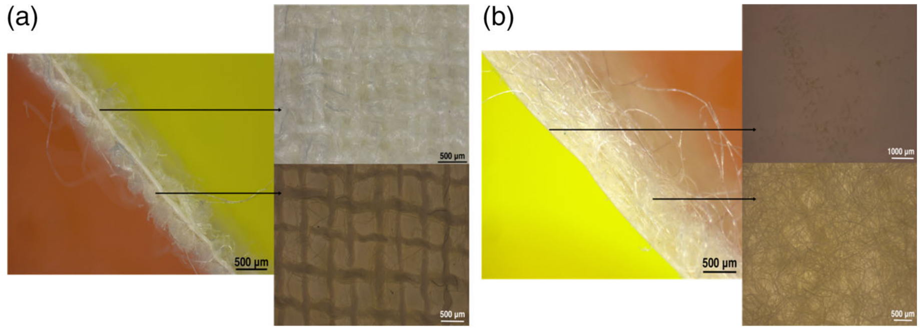


**FIGURE 3** Examples of moisture barriers used in firefighting clothing ensemble, (a) a three-layer moisture barrier with a woven fabric support, (b) two-layer moisture barrier with a non-woven fabric support. [Color figure can be viewed at wileyonlinelibrary.com]

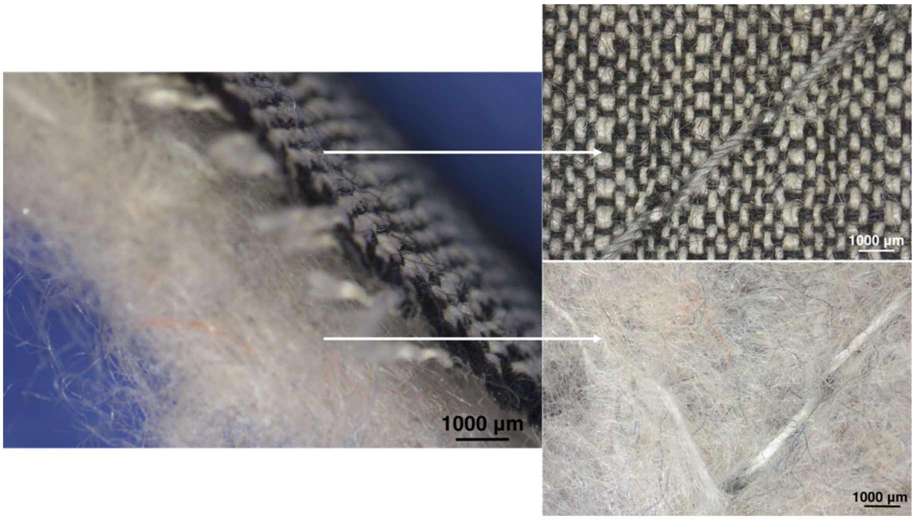


**FIGURE 4** Picture of a typical thermal liner used in firefighters' protective clothing (pictures on the right show the stitch line on both faces of the thermal liner). [Color figure can be viewed at wileyonlinelibrary.com]

fabric.[13] Examples of moisture barriers used in firefighters' protective clothing are shown in Figure 3.

Different types of membranes are used in moisture barriers for firefighters' protective clothing: semi-permeable, microporous, and non-porous.[4,14,15] In particular, a microporous membrane technology based on expanded polytetrafluoroethylene (ePTFE) developed by Gore-Tex is widely used as it combines heat and chemical resistance, liquid barrier, and water vapor permeability.[4] This ePTFE membrane contains more than nine billion pores, enabling the efficient transfer of moisture vapor. Other microporous membranes are made with FR polyurethane (PU) and polyvinylidene fluoride (PVDF).[14,16] It has also been proposed to use an electrospun nanofiber web cast on a woven fabric as a moisture barrier.[17] The membrane in the moisture barrier is usually laminated on a fabric substrate for mechanical support. These support fabrics use the same high-performance fibers found in firefighters' outer shell fabrics.[4]

The most inner layer of firefighters' protective clothing is the thermal liner. Its main role is to provide thermal protection.[7] The moisture barrier and thermal liner together provide approximately 75% of the total thermal protection.[12,18] The thermal liner of firefighters' protective clothing generally includes a nonwoven batting quilted on a thin woven fabric (Figure 4). Both layers are generally made from high-performance fibers such as para-aramid, meta-aramid, PBI, and PBO.[4] The "needle-punched" and "spunlace" nonwoven batting structures are mostly used for making thermal liners for firefighters' protective clothing. They hold a high amount of small air pockets to provide high thermal insulation. The face fabric of the thermal liner is engineered to allow moisture wicking and a smooth touch on the skin.[8,12]

High-performance fibers such as para-aramid, meta-aramid, co-polymers of aramid, PBI, and PBO are typically used in firefighters' protective clothing.[19,20] They offer exceptional performances in terms of resistance to heat and flame and mechanical strength thanks to the mainly aromatic structure of their constitutive polymers. However, these polymers may be vulnerable to the effect of long-term exposure to the different harsh conditions associated with the firefighter work, leading to polymer degradation.[21] For instance, the wavelengths corresponding to the bond energies of the amide group, which is found in para- and meta-aramids, are in the range of 300–400 nm[22]; therefore it can easily break down due to exposure to UVA light (315–400 nm) and UVB light (280–315 nm). Similarly, the PBO polymer has been found to be sensitive to UV radiation; in this case, the polymer goes through a photo-induced electron transfer reaction, which is self-sensitizing.[23] In addition, the benzoxazole ring found in the chemical structure of PBO is sensitive to hydrolytic degradation and eventually breaks down into aminophenol and benzoic acid due to prolonged exposure to moisture.[24] The physical structure of the high-performance fibers may also contribute to their degradation over time. For instance, micro voids are formed in the para-aramid fibers during their manufacturing, which facilitates the moisture absorption into the fiber structure.[25]

Polymer aging is defined as an unacceptable change in the material and its performance.[26] It may happen during the manufacturing process, storage and end-use, and may result in a change in the physical and/or chemical properties of polymers. The polymer may undergo physical aging, chemical aging or both of these.[27] Slater[28] described the effect of polymer degradation on textile materials. He identified two stages in the degradation process, which correspond to the visible and performance levels. Below the performance limit, the textile material loses its functional quality. On the other hand, the visible limit defines when visual cues of the materials' deterioration occur. However, the occurrence of visible signs of degradation like discoloration, fading, roughness, etc., does not always mean that the textile material has lost its functional quality. Alternatively, textile materials may lose their functional quality due to aging before any sign of degradation is visible.[29] As shown in Figure 5, this situation is associated with major concerns for the end-user safety in the case of protective clothing for instance.

In this article, a comprehensive review is provided of the aging behavior of high-performance fibers typically used in firefighters' protective clothing to respond to the research question of how the different aging conditions affect the performance of fire-protective fabrics. Section 2 describes the results of studies performed on used firefighters' bunker gear. Section 3 details the degradation mechanisms due to aging for a series of high-performance fibers relevant to firefighters' protective clothing. Section 4 examines the factors that affect the aging of firefighters' protective clothing. Section 5 briefly describes some of the models used for studying the aging behavior of firefighters' protective clothing and discuss their limitations when predicting materials' aging behavior using accelerated aging data. Finally, Section 6 identifies research gaps and some critical questions to be addressed.

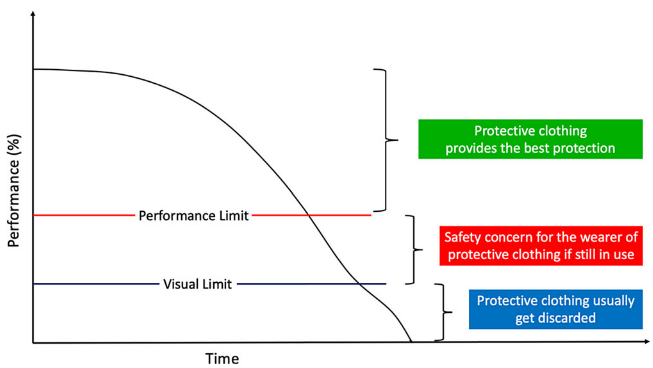


FIGURE 5 Evolution of the performance of textile materials as a function of time.[28] [Color figure can be viewed at wileyonlinelibrary.com]

## 2 | AGING OF FIREFIGHTERS' PROTECTIVE CLOTHING IN SERVICE

Researchers at the University of Kentucky conducted a series of studies on used firefighters' protective clothing.[30–33] They assessed the residual mechanical, barrier, and thermal performance of used turnout gear from career and volunteer firefighters. The garments were between 2 and 21 years old. Bunker suits were collected from career and volunteer firefighters to increase the sample size. Nothing was mentioned by the researchers regarding eventual differences between the career and volunteer firefighters bunker suits and the same models are expected to be used by both categories of firefighters. However, differences may exist in terms of the frequency of use and storage conditions among others.[34] For instance, although both career and volunteer firefighters execute comparable tasks, Hwang et al.[34] discovered that more than 50% of the volunteer firefighters in their study kept their bunker gear in their own vehicles while the protective equipment of career firefighters is usually stored at the fire station. Volunteer firefighters were also found to wear their uniforms for a much longer period of time (20–37 years) than career firefighters (12–15 years).

Table 1 provides a synopsis of the tests that were conducted in each of the four studies.[30–33] Most of the tests were performed on all layers of the garment.

In the first study, the researcher evaluated the conditions of used turnout coats based on the design and performance requirements of the NFPA 1971[35] standard specification.[33] For this study, they collected 20 used turnout coats from a fire department. The fiber content of the outer shell and moisture barrier support fabrics was para-aramid (Kevlar®) and meta-aramid (Nomex®). Seven of these turnout coats had been used for training purposes while the remaining 13 had been worn by career and volunteer firefighters. Among the 20 turnout coats studied, 14 had been in use for one to five years; the remaining six coats were more than five years old. For comparison purposes, the researcher also collected new

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**TABLE 1** Tests performed to evaluate the residual performance of used firefighters' protective clothing (Information from References 30–33).

| | | Test | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Study** | **Origin of the samples tested** | **Water absorption** | **Tensile strength** | **Water penetration** | **Water permeability** | **Tear strength** | **Flashlight test** | **Sewn seam breaking strength** | **Thermal protective performance** | **Char, heat and ignition resistance** | **Flame resistance** | **Total heat loss** | **Fabric weight** | **Fabric count** | **Fabric thickness** | **Visual inspection** | **Light evaluation** | **Leakage evaluation** | **Manikin test** | **Laundering cycles** |
| 33 | Outer shell only | √ | √ | | | | | | | | | | | | | | | | | |
| | Moisture barrier only | | | √ | √ | | | | | | | | | | | | | | | |
| | Thermal liner only | | | | | | | | | | | | | | | | | | | |
| | All layers | | | | | √ | | √ | √ | √ | √ | | √ | √ | √ | √ | | | | |
| 31 | Outer shell only | | | | | √ | | | | | | | | | | | | | | |
| | Moisture barrier only | | | √ | | | | | | | | | | | | √ | √ | | | |
| | Thermal liner only | | | | | | | | | | | | | | | √ | √ | | | |
| | All layers | | | | | | | √ | √ | | √ | √ | | | | | | √ | √ | |
| 32 | Outer shell only | | √ | | | √ | | √ | | | | | | | | | √ | | | |
| | Moisture barrier only | | | √ | | | | | | | | | | | | √ | √ | √ | | |
| | Thermal liner only | | | | | | | | | | | | | | | √ | √ | | | |
| | All layers | | √ | | | | | √ | √ | | √ | √ | | | √ | √ | | √ | | √ |
| 30 | Outer shell only | | | | | | √ | | | | | | | | | | | | | |
| | Moisture barrier only | | | √ | | | | | | | | | | | | | √ | √ | | |
| | Thermal liner only | | | √ | | | | | | | | | | | | | √ | √ | | |
| | All layers | | √ | | | √ | | √ | √ | | √ | | | | √ | √ | | | | |

fabrics of the same type as in the used turnout coats. The researcher assessed the residual mechanical, thermal, and water absorption performance of the turnout coats' outer shell fabric and moisture barrier using 13 different tests (Table 1). The properties measured included the tensile strength, tear strength, sewn seam breaking strength, heat resistance, flame resistance, and water absorption. For the moisture barriers, they additionally performed two types of water penetration tests: high pressure and low-pressure water permeability. The researcher also measured the weight, fabric count, and thickness of the fabrics, as well as the thermal protective performance (TPP) of the whole clothing assembly. In addition, they performed the visual and microscopic examination of the used protective coats and measured the coefficient of retro-reflectivity of the reflective trim.

All the outer shell specimens passed the heat, flame and thermal resistance test according to the requirements of NFPA 1971, 1991 edition.[33] In the case of the tensile strength test, the researcher performed the test both on dry and wet fabrics. Two outer shell fabrics out of 20 fabrics did not pass the tensile test performed on dry fabric. One of the corresponding turnout coats had been used for less than five years. Moreover, five outer shell fabrics out of the 20 turnout coats tested did not pass the tensile test performed on wet fabric specimens. Among these five turnout coats, two had been used for firefighting activities between one and five years. The other three turnout coats out of the five that failed to meet the wet tensile test requirement had been used only for training purposes; one garment had been used less than five years. In the case of the water absorption resistance test, eight fabrics out of the 20 tested failed the test. Among these, five fabrics had been used for training purposes, and the remaining three fabrics had been used for firefighting purposes. Among the five coats that had been used for training and failed the water absorption resistance test, three of them were between one and five years old. All three coats that were used for firefighting purposes and failed the water absorption resistance test were less than five years old. The researcher hypothesized that a large amount of abrasion in the used firefighter turnout coats could be a reason for the losses in properties like fabric strength and water resistance.

All the used moisture barriers passed the tear, heat, and thermal resistance test.[33] In terms of flame resistance, eight moisture barriers failed to meet the char length requirement and four failed to meet the after-flame requirement. In the case of the high-pressure water penetration test, the author reported the failure of 14 used moisture barriers out of the 19 tested. Ten of these 14 moisture barriers had been used in firefighting operations between one and five years. Eight moisture barriers out of the 19 tested failed the low-pressure water penetration resistance test. Among them, five had been used in firefighting operations between one and five years. Abrasion was mentioned by the researcher as the main contributor to the deterioration of the barrier performance of the moisture barriers. On the other hand, aging did not appear to strongly affect the tear strength of the moisture barriers. All the moisture barrier specimens met the minimum tear strength requirement (5 lb) by NFPA 1971.

A second study conducted a few years later involved a larger sample size with 71 career firefighters' turnout gear.[31] They were collected from medium and large fire stations and covered four age categories: 2–3 years, 5–7, 9–10 years or retired. The outer shell of the suits was constructed from various bends of para-aramid, meta-aramid, and PBI fibers, while the moisture barrier was an ePTFE membrane laminated to a meta-aramid fabric support. The suit assembly also included an aramid fiber batting in the thermal liner. For the evaluation of the samples, the researcher followed the 2008 edition of NFPA 1851 for the inspection protocol and the 2007 edition of NFPA 1971 for the performance assessment (Table 1). The thesis work aimed at putting to the test the useful time of 10 years for turnout gear recommended in NFPA 1851 and compare the laboratory test results with the NFPA 1851 inspection protocol. All 71 protective suits went through visual inspection by the researcher before any destructive test was performed. Flame and tear resistance tests were conducted on the outer shell fabric of the aged fire-protective suits whereas water penetration evaluation was performed on the moisture barriers. The author also did the light and leakage evaluation of the thermal liner of these protective suits. Besides, they measured TPP and total heat loss (THL) on the whole clothing assembly of the aged firefighters' protective clothing and sewn seam strength on the individual layers.

Upon visual inspection, the researcher found holes, signs of abrasion, and thin spots on about 20% of the outer shells.[31] More than 8% of the outer shell fabrics and 11% of the thermal liners had poor cleaning. No moisture barrier was found to be in excellent cleaning conditions. Ten garments failed the light evaluation test: seven pants and three coats. The researcher noted that failures mostly occurred in the crotch and seat areas of pants. Surprisingly, they found more thin spots in 2–3-year-old garments compared to older garments. The leakage evaluation test was performed on 67 garments: 22 failed the test. The author observed that the majority of the failures were in the garments' seam area.

The manikin test was performed on two garments that had been in use for one year and were exposed to a chemical fire.[31] The results revealed excellent thermal protection of the aged garments. Furthermore, all the aged garments tested passed the TPP test. The author found an increase of more than 20% on average in the TPP value of the used garments compared to the new ones. It was attributed to the increased thickness of the garments over time. In the case of THL, only one of the 9-10-year-old/retired suits failed to meet the NFPA 1971[36] requirements. All the aged outer shell and thermal liner samples from all age categories passed the flammability test. Only a moisture barrier sample from the 9–10-year-old/retired category failed the flammability test.

On the other hand, the researcher noticed considerable tear strength reduction in the aged fire-protective suits.[31] For instance, they recorded an average tear strength of 40.3 lbf for the 2-to-3-year-old para-aramid/PBI blended outer shell while it was on average equal to 29.4 lbf for the 9-to-10-year-old outer shells with the same fiber content. Among all the tested garments, they found that one 2-to-3-year-old and one 9-to-10-year-old/retired outer shell did not meet the NFPA 1971 (2007) requirement in terms of tear strength. Based on the comparison of the results between the different fiber contents, the researcher concluded that the para-aramid/meta-aramid blended fabrics best preserved their performance over the long term.[31]

In the third study of this series, the researcher collected 76 firefighters' turnout gear from volunteer firefighters.[32] The fiber blends found in the outer shell fabrics included para-aramid, meta-aramid, and PBI. The moisture barrier was an ePTFE membrane laminated on a woven or non-woven meta-aramid/para-aramid fabric, while the thermal liner was made of E-89 or aramid fibers. They also tested samples from the garments of the previous study (except for four garments that were not available for further investigation) to increase the sample size. The aim of this third study was to find out the effect of maintenance procedures on the performance and durability of both career and volunteer firefighters' turnout gear.

All the tests that were conducted in the previous study were also performed on the samples collected for this study.[32] In addition, the researcher conducted thickness measurements and a laundering test on the used firefighter's turnout gear. They also used a list of questions to document the use and care of the garments performed by the firefighters. The researcher found that with the increase in washing cycles, the THL value decreased while the TPP value increased, which indicates the importance of proper care of turnout gear. Also, they found a positive correlation between the thickness and TPP of the turnout gears. Overall, the TPP, THL, and flammability results met the NFPA 1971 requirements and supported the recommended ten years of useful time. On the other hand, the tear, tensile, and seam breaking strength and the hydrostatic testing did not meet the minimum requirements for some of the suits aged less than ten years. For instance, about 11% of the tested outer shells (15 out of 143) did not meet the minimum breaking strength requirement of NFPA 1971, 2007 edition. In addition, three of the 19 outer shell specimens that were four years old or less did not meet the NFPA 1971 requirement for tear strength. About 11% of the outer shell samples failed the seam-breaking strength requirement. The survey also revealed that not all firefighters followed the recommended maintenance procedure for their turnout gear, which could be a reason for the deterioration observed on the used turnout gears.

For the last study of this series, the researcher collected 108 retired firefighter's garments that were older than the firefighting garments collected in the previous three studies.[30] The bunker suits were classified into three age groups: 10–12 years old, 13–17 years old, and 18–21 years old. The outer shell fabrics of these garments were blends of para-aramid, meta-aramid, and PBI fibers in different ratios. Depending on the case, the suits had an ePTFE-based moisture barrier with a meta-aramid/para-aramid blend fabric support (Crosstech® and Goretex®) or a polyurethane-based moisture barrier (Aquatech®). The thermal liner was made of aramid fibers. The tensile strength test was conducted only on the outer shell specimens, while the tear resistance, seam breaking strength, and flammability tests were measured on all three layers (outer shell, moisture barrier, thermal liner) of the garment (Table 1). Besides, the TPP and thickness were measured for the whole garment assembly. The aim of the work was to evaluate the ten-year retirement age, and the care and maintenance of firefighter's turnout gear.

Among the 108 garments collected, the researcher identified 40 garments in "poor or extremely poor" condition (Reference 30, p-43). The researcher also noted the presence of holes, rips, cuts, and tears in the outer shell of more than 75% of the 108 retired garments. Destructive tests (TPP, thickness, tear resistance, seam breaking strength, flammability, and tensile strength) were performed on specimens from the 40 most damaged garments. All the samples passed the minimum requirement specified for TPP in NFPA 1971, 2007 edition. The researcher confirmed the interaction between the garments' thickness and the TPP results first reported by Trenkamp.[32] On the other hand, 75% of the outer shells tested failed to meet the tear strength requirement of NFPA 1971, 2007 edition.[30] Using a one-way ANOVA, the researcher found that the outer shells made from para-aramid/meta-aramid exhibited significantly higher tear resistance retention compared to the para-aramid/PBI outer shell fabrics. Almost 50% of the outer shells tested also failed to meet the NFPA 1971, 2007's minimum requirement for tensile strength. Like for the tear strength results, the researcher noticed a significantly higher tensile strength for para-aramid/meta-aramid outer shells compared to para-aramid/PBI outer shell fabrics. For the seam breaking strength, which was measured on 14 outer shell garments, only 7% of the samples could not meet the minimum requirement of the NFPA 1971, 2007 edition. On the other hand, all of the outer shells tested passed the flammability test. The researcher's conclusion was that after ten years, the turnout gear has lost its functional property that is needed for proper protection of the firefighters.[30]

Figure 6 shows a compilation of the tear force data of outer shells obtained in the four different studies as a function of the garment age. The data are identified in terms of the fabric fiber content (meta−/para-aramid and para-aramid/PBI) and the type of firefighters (career and volunteer). A decrease in the tear force with the garment age can be observed for all conditions. A gray line on the figure identifies the NFPA 1971 requirement of 22 lb for the tear force. As the age of the garments increases, a higher number of them do not meet the tear force requirement. However, even for protective garments less than ten years old, which is the NFPA recommended retirement age for bunker suits, several failures to meet the requirement were observed, in particular with volunteer firefighter bunker suits.

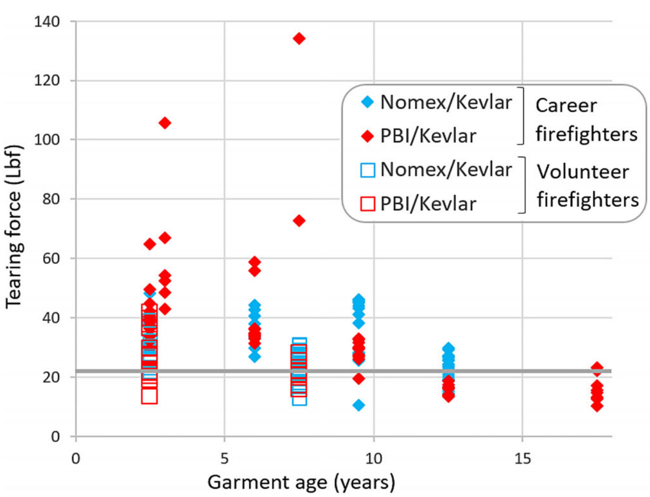


FIGURE 6 Variation of the tearing force of Nomex/Kevlar and Kevlar/PBI outer shells as a function of the garment age for used firefighter bunker suits used by career and volunteer firefighters (data from Reference 37). The gray line indicates the NFPA 1971 requirement (22 lb). [Color figure can be viewed at wileyonlinelibrary.com]

## 3 | AGING OF HIGH-PERFORMANCE FIBERS USED IN FIREFIGHTERS' PROTECTIVE CLOTHING

This loss in performance observed in used bunker suits can be attributed in part to the degradation experienced by high-performance fibers due to continuous exposure to hazardous conditions. This section briefly describes the aging mechanisms of some high-performance fibers that are used in firefighters' protective clothing currently on the market: para-aramid, meta-aramid, Technora®, PBO, PBI, and Liquid Crystal Polyester (LCP). It may be noted that LCP fibers are the only fibers from this list that are not inherently flame resistant.

### 3.1 | Aging of para-aramid fibers

Although para-aramid fibers (Figures 7 and 8) exhibit superior quality compared to conventional fibers, their performance gets affected over time due to exposure to various hazardous conditions. For instance, several researchers have reported the premature aging of para-aramid fibers due to exposure to accelerated thermal conditions. Arrieta et al.[38] observed changes in the chemical structure and mechanical properties of para-aramid/PBI blended fire-protective fabrics after exposure to temperatures ranging between 190°C and 320°C. Although the continuous operating temperature of para-aramid fibers has been reported to be 190°C and that of PBI to be 200°C,[11] the para-aramid/PBI fabric lost 50% of its breaking force after 12 days of exposure at 190°C.[38] A follow-up study by the same group of researchers showed that thermal aging caused a crystalline lattice disruption across the perpendicular direction of the para-aramid fibers' coplanar sheets, whereas the crystallinity increased along the coplanar sheets.[39] Ozgen & Pamuk[40] also demonstrated the negative effect of thermal aging on para-aramid fibers. They subjected a 100% para-aramid fabric to thermal aging at 220 and 300°C for up to 30 and 10 days, respectively. They observed a loss in the breaking force of the para-aramid fabrics of more than 50% after exposure to 220°C for two days only. Eventually, the fabric lost more than 90% of its strength after 30 days at 220°C.

The para-aramid fiber also gets severely affected by exposure to UV radiation.[41–45] UV light, either natural or artificial, contains high energy photons and can easily decompose and degrade organic compounds.[46] UV light with a wavelength between 290 and 400 nm possesses a high enough energy to break the polymers' chemical bonds and forms a free radical that initiates a

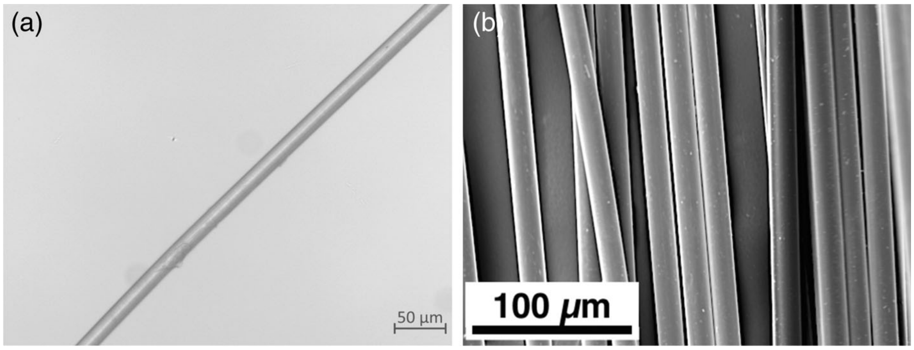


**FIGURE 7** Microscopic images of para-aramid filaments, (a) optical microscopy image, (b) scanning electron microscopy (SEM) image.

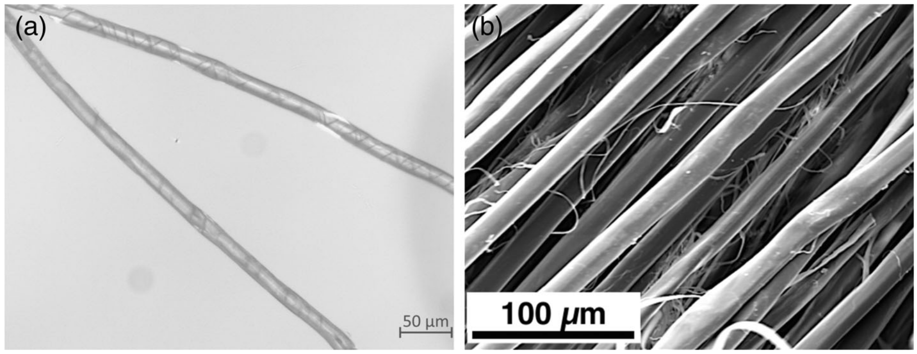


**FIGURE 8** Microscopic images of para-aramid staple fibers, (a) optical microscopy image, (b) scanning electron microscopy (SEM) image.

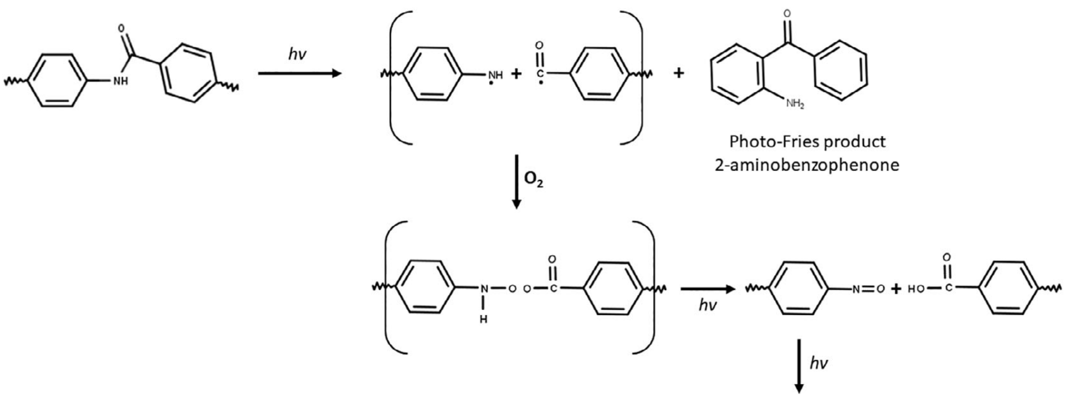


**FIGURE 9** Possible UV degradation mechanism of para-aramid fibers. Reproduced with permission.[41] Copyright 2011, Elsevier.

chain reaction.[47] It may be noted that UV light with a wavelength lower than 280 nm is generally absorbed by the atmosphere and does not reach the surface of the earth.[48]

The susceptibility of the para-aramid fiber to UV light is possibly attributed to its aromatic structure.[47] Para-aramid fibers absorb a high amount of UV light, which leads to an oxidative reaction and subsequently causes color changes and, most importantly, reduces the fiber properties.[4,49,50] Figure 9 shows a possible UV degradation mechanism of para-aramid fibers.

Arrieta et al.[41] exposed a para-aramid/PBI fire-protective fabric to different accelerated UV aging conditions for up to 35 days using a Xenon weatherometer. The irradiance ranged between 0.35 and 1.55 W/m$^2$ (measured at a wavelength of 340 nm) and the temperature was comprised between 50 and 80°C. The residual mechanical performance was assessed by performing a tensile strength test on yarns raveled from the UV-aged fabric specimens. The researchers reported a 50% loss in the yarns' tensile strength upon exposure to the longest UV exposure time (840 h). ATR-FTIR (Attenuated Total Reflection- Fourier Transform Infrared Spectroscopy) analysis of the UV-aged specimens found evidence of cleavage in the amide linkage of the para-aramid fibers. This demonstrated the occurrence of photo-oxidation in the UV-aged specimens, to which the specimens' loss in the force at the break was attributed. In another study, Houshyar et al.[51] investigated the UV aging behavior of a para-aramid/PBI blended fabric. They observed a 79% reduction in the fabric's tensile strength after subjecting it to 0.24 $W/m^2$ irradiance (measured at 340 nm) at 40°C and 50% relative humidity for seven days.

Fire-protective fabrics with different contents of para-aramid fibers also exhibited compromised performance while exposed to hydrothermal aging conditions. Arrieta et al.[41] reported a 50% loss in the force at the break of a para-aramid/PBI blended fabric after exposing them to high humidity conditions at elevated temperature (60% RH, 80°C) for 31 days. The researchers mentioned the sensitivity of para-aramid fibers to hydrolysis in acidic conditions as the possible culprit for the loss in strength in the aged fabric. In fact, the para-aramid fiber contains amide groups in its chemical structure, which are susceptible to hydrolysis.[52] Engelbrecht-Wiggans et al.[53] observed a 14% reduction in para-aramid yarn's tensile strength after being exposed to 76% RH at 70°C for one year. The reason for the larger decrease in mechanical performance of para-aramid/PBI fabrics compared to other fiber blends with a similar para-aramid content was elucidated by Hoque et al.[54] They uncovered that sulfur present in the PBI fibers as a residue of the manufacturing process creates an acidic environment for the para-aramid fibers and accelerates their degradation via hydrolysis.

Fabrics containing para-aramid fibers were also severely affected by repeated launderings. Dolez & Malajati[55] subjected a 100% para-aramid fire-protective fabric to up to 50 washing/drying cycles performed according to NFPA 1971.[7] They observed a gradual decrease in the tear strength of the specimens with increased laundry cycles. The fabric lost almost 40% of its strength after only ten laundering cycles and nearly 60% of its original tear strength after 50 laundry cycles. Other fabrics containing different percentages of para-aramid fibers along with meta-aramid, PBI, Basofil, and PBO fibers were affected to different degrees by the repeated launderings. With the exception of a fabric containing a blend of para-aramid, meta-aramid, and PBO, all fabrics containing 60% of para-aramid or more were severely affected by the repeated launderings.

## 3.2 | Aging of meta-aramid fibers

Several researchers have studied the aging behavior of fire-protective fabrics containing meta-aramid fibers.[51,56–61] For instance, Dolez et al.[59] investigated the accelerated thermal aging behavior of a 100% meta-aramid fabric. The researchers subjected fabric specimens to temperatures ranging between 150 and 300°C for up to 500 h. Although the fabric retained 80% of its tearing force after aging at 150°C for 500 h, it lost 20% of its tearing force after only 1 h at 300°C. In another study, Rezazadeh[62] exposed meta-aramid-dominated fire-protective fabrics to different heat fluxes ranging between 10 and 40 $kW/m^2$ and examined the color fading and mechanical performance after radiant heat exposure. They observed a considerable deterioration of the fabrics' tensile strength after exposure to 20 $kW/m^2$ heat flux for 300 s.

Meta-aramid fibers (Figure 10) are known to be sensitive to prolonged exposure to UV radiation.[63] The long-time exposure to UV light causes the color to fade and results in a severe loss in the fiber's mechanical performance. The fiber's manufacturer suggests keeping meta-aramid fiber-based fabrics away from light during storage. However, the fabrics may still be exposed to UV during service. Houshyar et al.[60] examined the UV aging behavior of 100% meta-aramid fabrics. The fabric specimens were subjected to 0.24 $W/m^2$ irradiance at 340 nm at 40°C and 50% RH for up to 7 days. After seven days of continuous UV exposure of the fabrics, the researchers found an 84% decrease in the tear strength of the specimens. A rapid degradation was observed during the first three days of UV exposure, with a 36% decrease in the fabric's tear strength. In addition, the author found evidence of broken fibers in the UV-aged specimens. In another study, Nazaré et al.[61] subjected meta-aramid-dominated fire-protective fabrics to UV irradiation at 15.9 $kJ/m^2$ at 340 nm at 50°C and 50% RH for up

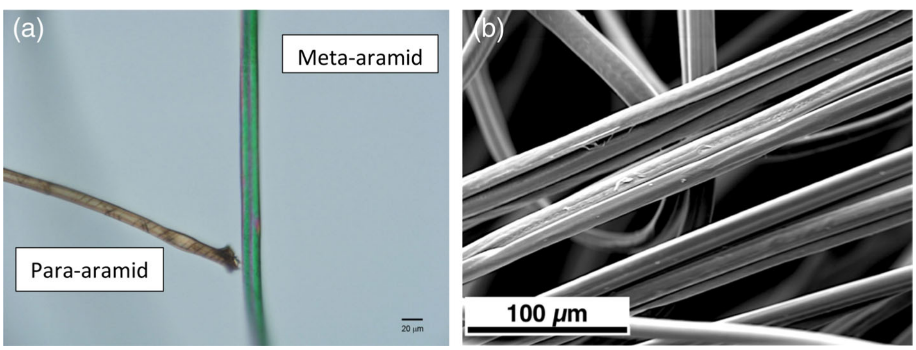


FIGURE 10 Microscopic images of meta-aramid staple fibers, (a) optical microscopy image, (b) SEM image. [Color figure can be viewed at wileyonlinelibrary.com]

to 66 days. They found an 80% decrease in the tear strength of the fabric after 14 days of exposure. Though the initial decrease in the tearing force was rapid, the fabric degradation slowed down with further exposure. A 95% decrease of the tearing force was found after 56 days of exposure to the UV aging condition. Day et al.[58] exposed high meta-aramid content fire-protective fabrics to 0.75 $W/m^2$ at 420 nm for 40 h with black and silver panel temperatures of 60°C and 42°C, respectively. During the UV exposure, 30% RH was maintained in the equipment. They observed a 40% decrease in the fabric tear strength due to UV aging. However, they did not observe any significant changes in the fabric flame resistance and TPP due to UV aging. Figure 11 illustrates a proposed mechanism of UV degradation of meta-aramid fibers.

Meta-aramid-based fire-protective fabrics have been observed to exhibit a strong resistance to hydrothermal aging under immersed conditions.[54] In comparison with para-aramid fibers, meta-aramid fibers are less prone to hydrolysis.[55] The flexible structure of the meta-aramid molecule allows a closer packing that restricts the penetration of water molecules in its fine structure.[65] Meta-aramid-dominated fire-protective fabrics have also been found to resist well to repeated launderings. Dolez & Malajati[55] subjected a 100% meta-aramid fabric to 50 washing/drying cycles. The fabric did not exhibit any loss in tearing force, even after 50 washing/drying cycles.

## 3.3 | Aging of fibers made of copolymers of aramid with large diamines (Technora®)

Although the Technora® fiber (Figure 12) came to the market in 1985,[11] the literature regarding its aging behavior is still very limited. The Mars Science Laboratory (MSL) studied the aging behavior of the Technora® fiber during storage.[66] They kept a parachute in a deployment bag for over three years. Technora® fiber-based yarns

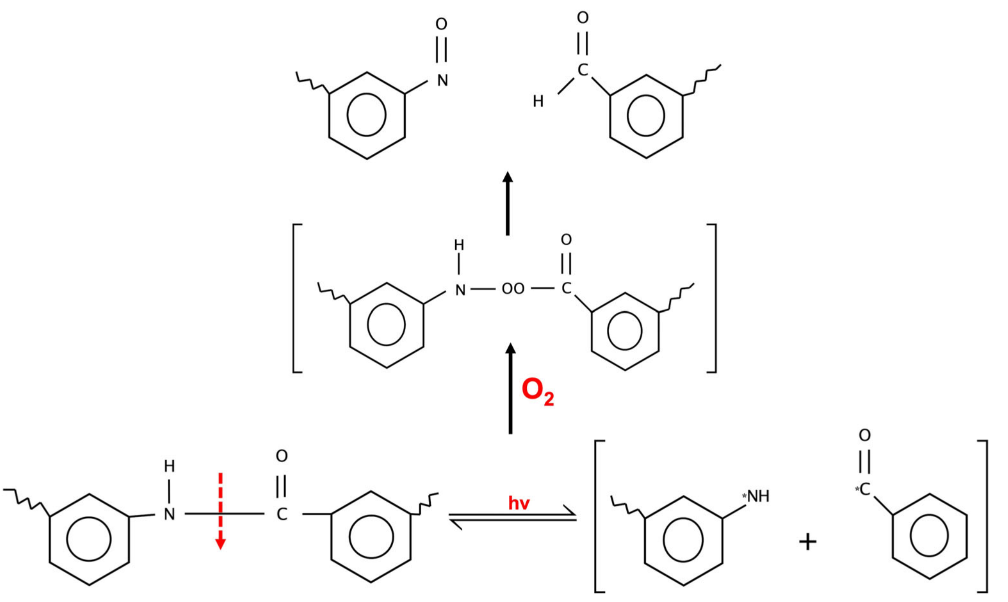


FIGURE 11 Possible UV degradation mechanism of meta-aramid fibers. Reproduced with permission.[64] Copyright 2013, Elsevier. [Color figure can be viewed at wileyonlinelibrary.com]

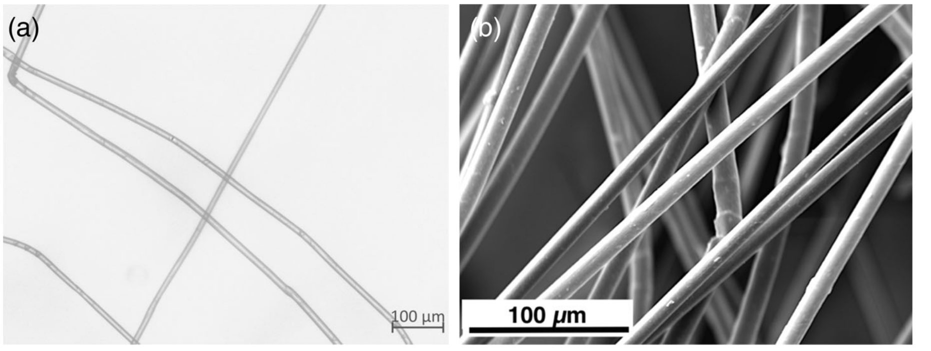


FIGURE 12 Microscopic images of Technora® staple fibers, (a) optical microscopy image, (b) SEM image.

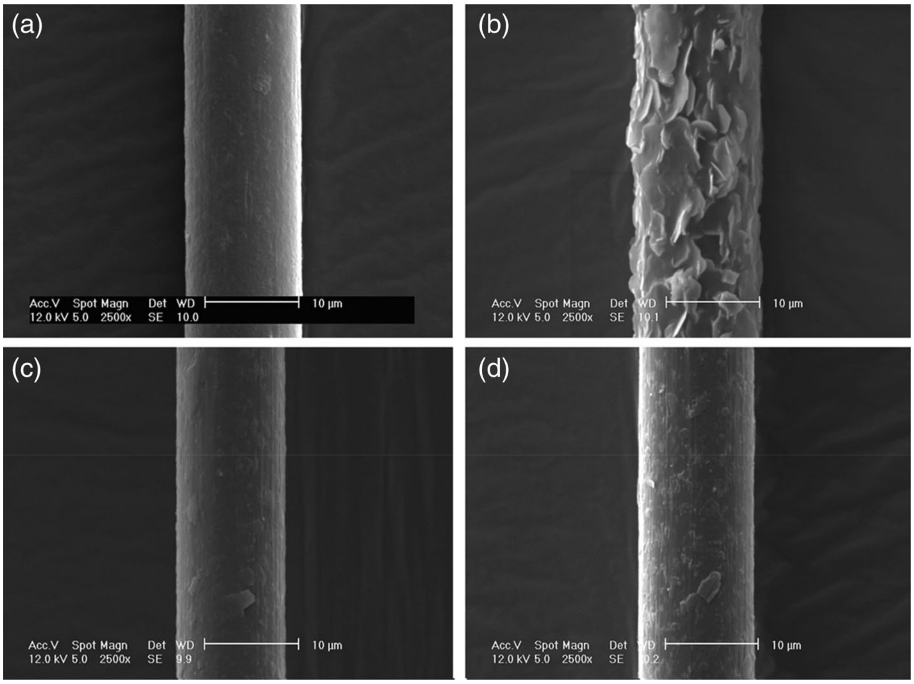


**FIGURE 13** SEM images of unaged Technora® fiber (a) and after one year of aging, (b) 80°C, pH 11; (c) 80°C, pH 9; (d) 80°C, deionized water (Reproduced with permission from Reference 67).

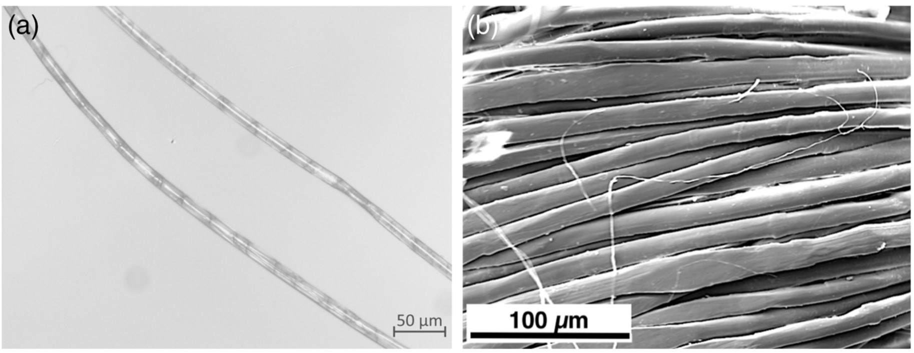


**FIGURE 14** Microscopic images of PBO staple fibers, (a) optical microscopy image, (b) SEM image.

were used to join different parts of the parachute. The researchers measured the residual seam and joint strength every six months. The researchers reported conflicting results, with an increase in strength in some joints while a significant reduction was observed in other joints. They attributed the variable results to challenges and limitations in the study design and test conditions.

In another study, Derombise et al.[67] investigated the hydrolytic aging behavior of Technora® fibers after subjecting them to different aqueous solutions. The researchers used a 1670 dtex Technora®-based yarn. The specimens were immersed in three types of solution – (i) deionized water, (ii) pH 9 buffer solution, and (iii) pH 11 buffer solution - at 20, 40, 60, and 80°C for one and a half years. Both buffer solutions were made using sodium carbonate salt. They reported a very slight decrease in the yarn's tensile strength (~ 4%) after one and a half years of aging at the worst condition (80°C, pH 11). On the other hand, they observed some changes in the fiber morphology (Figure 13) after one year of aging in the pH 11 solution at 80°C, which were attributed to a rearrangement in the finish at the fiber surface. In addition, through FTIR analysis, they found a decrease (0–5%) in the amide I peak for all the conditions studied. Overall, the authors concluded that Technora® is highly stable in alkaline and neutral aqueous solutions at elevated temperature. This finding also echoes the study by Imuro & Yoshida.[68] The authors found that the tensile strength of Technora® fiber (HM-50) did not significantly decrease after exposure to a 120°C saturated steam for 400 h.

### 3.4 | Aging of PBO fibers

Although the PBO fiber (Figure 14) shows superior mechanical and thermal performance, it is sensitive to light and moisture. In humid conditions, the fiber strength decreases at high temperatures, even less than 100°C.[69] A small level of light exposure also decreases the fiber strength significantly. The UV aging of PBO fiber was shown to accelerate in the presence of moisture.

Researchers have examined PBO yarns aged under elevated temperature and moisture levels and analyzed the fibers' chemical, morphological, and mechanical changes.[24] The tensile strength of PBO fiber-based yarns decreased by approximately 30% upon exposure to 50°C and 60% RH for the first 84 days of aging, followed by 60°C and 37% for the remaining 73 days. By comparison, when the PBO fiber-based yarns were stored in ultra-dry conditions for 47 weeks, no change in tensile strength was observed. Furthermore, the researchers also sealed PBO yarns in a tube and subjected it to 55°C for 30 weeks. This time, the yarns' tensile strength decreased only by less than 4%. FTIR-ATR analysis showed that exposure of the PBO yarns to extreme heat and moisture changed the chemical structure of the fiber, to which the reduced mechanical strength measured was attributed. The researchers observed that the benzoxazole ring opened after the accelerated hydrothermal aging, introducing an amide functionality, followed by the hydrolysis of the amide to carboxylic acid and aminophenol groups. Figure 15 shows the degradation mechanism of PBO fibers under heat and moisture conditions.[24]

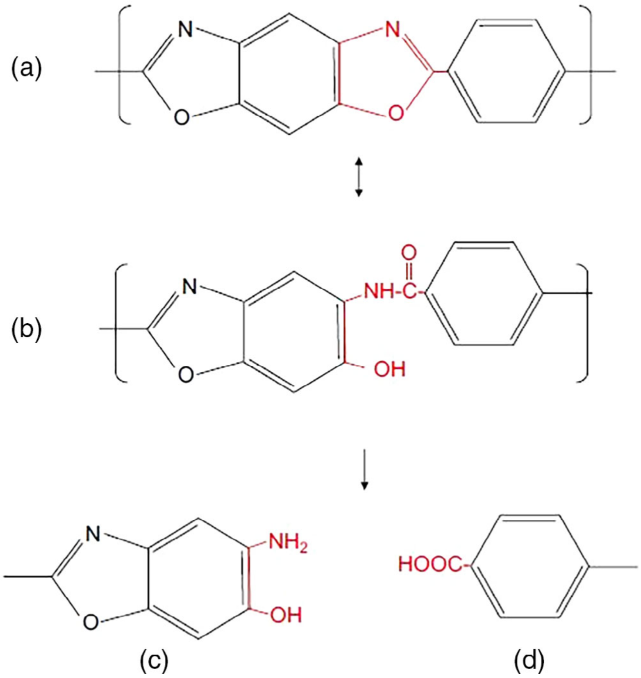


**FIGURE 15** Possible hydrolytic degradation mechanism of PBO fiber - benzoxazole ring affected by moisture (a), leading to the formation of benzamide (b); byproducts of benzamide hydrolysis: aminophenol (c) and benzoic acid (d). Reproduced with permission.[24] Copyright 2007, Elsevier. [Color figure can be viewed at wileyonlinelibrary.com]

Walsh et al.[70] investigated PBO fibers' moisture and UV aging. For the hydrothermal aging, the researchers immersed tows of PBO fibers in deionized water and kept them in an oven at 50°C. Another sample was prepared, exposed to water vapor (90% RH) only, and kept in an oven at 50°C. In addition, they also exposed PBO fibers to acidic water (0.5 M, 1 M, and 1.8 M phosphoric acid) at 20°C. They conducted the hydrothermal aging for up to 120 days. For the UV aging, PBO fiber samples were subjected to 750 $W/m^2$ irradiance (measured at 300–800 nm) using a xenon-arc lamp at 50°C. The tensile test data of the hydrothermally aged specimens showed a decrease in the force at break with increased aging time both in the case of water immersion and exposure to atmospheric moisture. The researchers also found evidence of a change in the fiber morphology (Figure 16) due to hydrothermal aging. In terms of the effect of UV aging, the authors reported that the PBO fibers started losing strength after 100 h of UV exposure; eventually, the aged

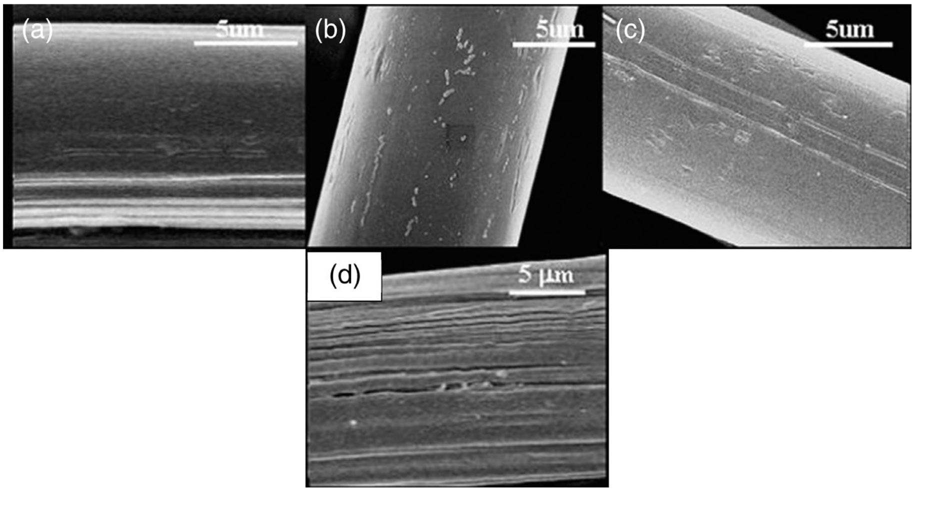


**FIGURE 16** SEM images of PBO fibers: unaged (a), aged in DI water (b), aged in 90% RH (c) and aged in 1.8 M phosphoric acidic water (d). Reproduced with permission.[70] Copyright 2006, John Wiley and Sons.

fibers lost 40% of their tensile force after 300 h of aging. They also observed changes in the fibers' surface morphology due to UV aging.

Niu et al.[71] studied the aging behavior of PBO fibers under light exposure. The researchers stored fiber samples in a black plastic bag and in a transparent plastic bag. They kept these bags three meters from a laboratory light for up to 8 years. The researchers did not find any significant loss in tensile strength for the samples aged in a black bag for eight years, indicating an excellent shelf life of the PBO fibers. On the contrary, the PBO fibers that were kept in the transparent bag lost 37% of their tensile strength after six months of exposure, indicating the sensitivity of PBO fibers to light.

Yehia[72] conducted a thorough investigation on the aging behavior of a 100% PBO fabric. The author subjected fabric specimens to heat, UV (fluorescent lamp), hydrothermal conditions, and repeated laundering cycles. The effect of thermal aging was assessed by subjecting the specimens to 235°C for 42 h. Fabric specimens were exposed to 80°C and 1 $W/m^2$ irradiance at 340 nm to assess the effect of UV aging. Hydrothermal aging conditions were applied by immersing the specimens in a water-containing flask and keeping it in an air circulating

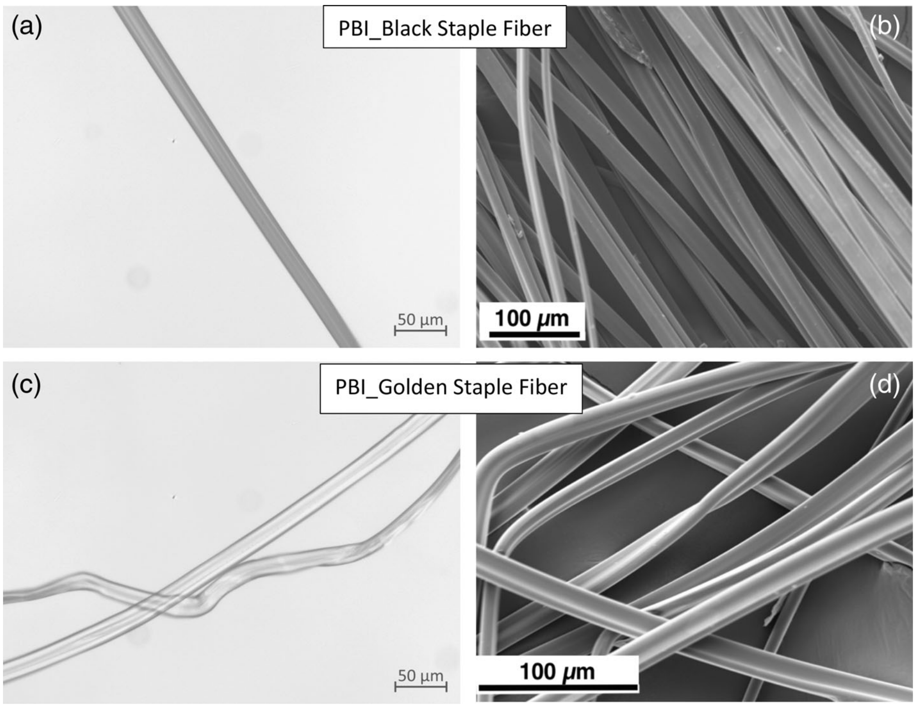


**FIGURE 17** Microscopic images of PBI black and golden staple fibers, (a) and (c) optical microscopy image, (b) and (d) SEM image.

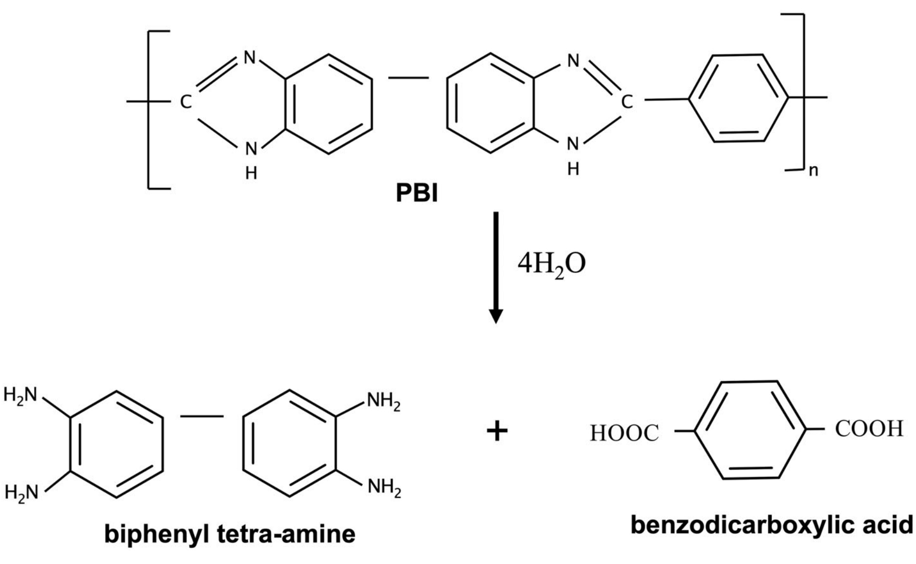


**FIGURE 18** Possible degradation mechanism of PBI under 300°C brine condition. Reproduced with permission.[74] Copyright 2004, Elsevier.

oven at 80°C for up to 31 days. A launderometer was used to subject fabric specimens to multiple washing for up to 10 cycles. The researcher measured the residual tear strength of the aged specimens to evaluate the effect of aging on the mechanical performance of the fabric. In this case, the 100% PBO fabric used in Yehia's[72] study resisted relatively well the hydrothermal aging and repeated laundry conditions, with only a 23 and 15% loss in tearing force, respectively, for the longest exposure. On the other hand, the loss in tearing force was 49 and 72% due to exposure to thermal and UV aging, respectively.

Useful information can also be extracted from a study by Fu et al.[73] on the hydrolytic degradation mechanisms of PBO film sheets. They synthesized PBO film sheets in the laboratory and exposed them to neutral and acidic (0.02 N and 0.2 N $H_2SO_4$) hydrothermal conditions for up to 25 days. They assessed the chemical changes in the PBO films due to aging using molecular mass and FTIR spectroscopy. The intrinsic viscosity of the aged samples showed an initial decrease during 16 days in neutral water before reaching a plateau. It took five days to reach the plateau for the sample aged in acidic water. This behavior does not appear to agree with the ring opening mechanism of PBO previously proposed in the case of hydrolytic aging as the intrinsic viscosity would keep reducing until most of the benzoxazole rings are opened. Furthermore, based on the FTIR analysis they performed, the authors concluded that the prime hydrolytic degradation mechanism of PBO is rather the chain session of o-hydroxy amide linkages in the PBO chemical structure.

## 3.5 | Aging of PBI fibers

With an entirely aromatic structure, the PBI fiber (Figure 17) is expected to perform better against hydrolysis and photochemical aging compared to other high-performance fibers.[41] However, most of the aging studies of PBI fibers found in the literature involved fabrics where PBI was in blends with other fibers. Therefore, it is not easy to extract the exact aging behavior of PBI fibers. However, in one study, researchers examined the hydrothermal degradation of a PBI coating on steel.[74] They found that under 300°C brine conditions, the PBI film underwent hydrolysis. Figure 18 shows the degradation mechanism proposed for PBI under brine conditions. Hydrolysis breaks the imidazole ring in the chemical structure of PBI and creates biphenyl tetra-amine and benzodicarboxylic acid, followed by a decrease in the thermal stability of the material. This hydrolysis also makes PBI more vulnerable to moisture.

In another study, Musto et al.[75] investigated the thermo-oxidative degradation behavior of a PBI film. They prepared a polymeric film (approximately 20 μm) from PBI powder. To examine the thermo-oxidative

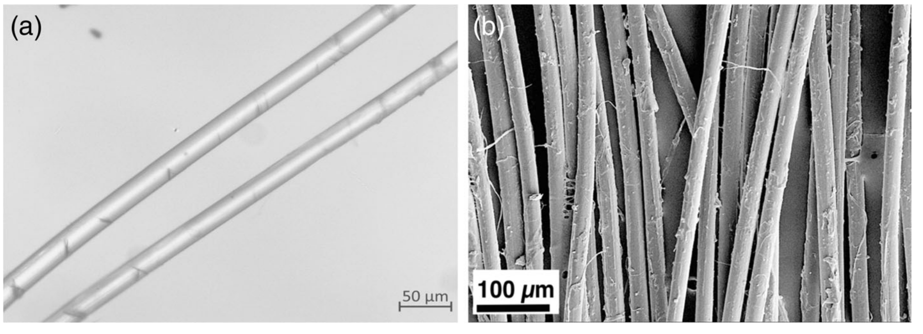


**FIGURE 19** Microscopic images of LCP fibers, (a) optical microscopy image, (b) SEM image.

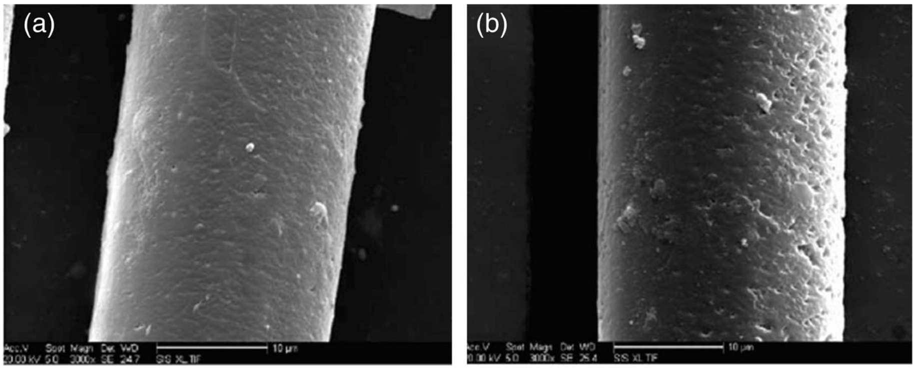


**FIGURE 20** SEM images of unaged (a) and UV aged-186 h (b) Vectran™ HT fiber. Reproduced with permission.[76] Copyright 2011, John Wiley and Sons.

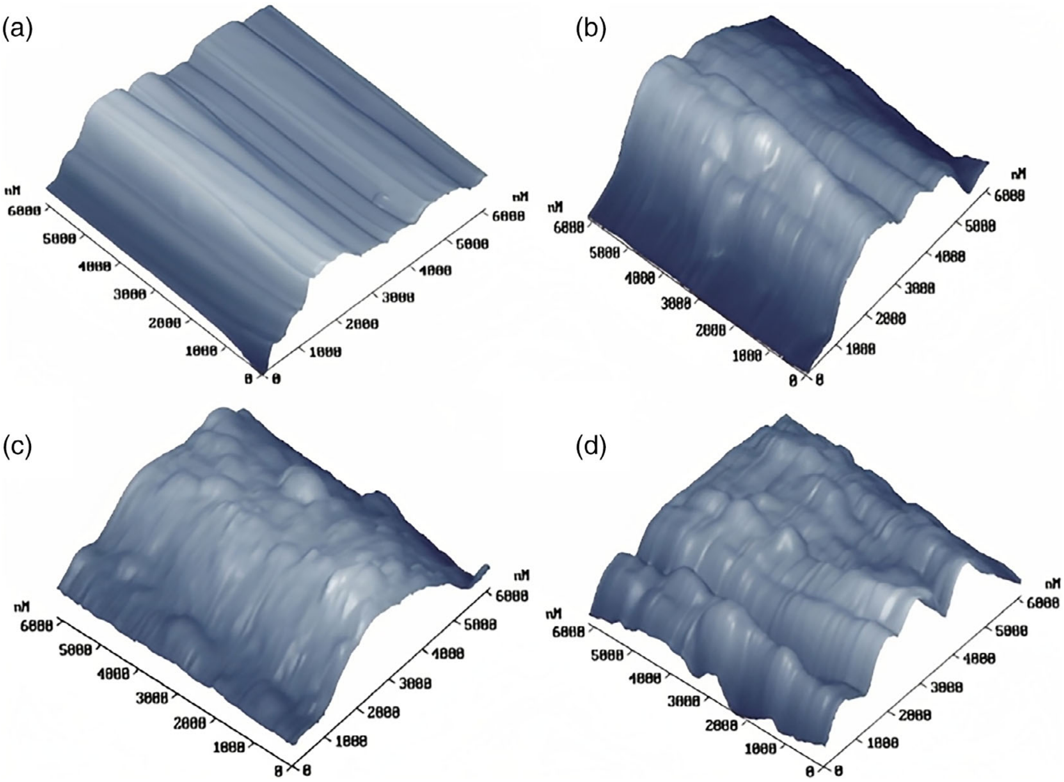


FIGURE 21 AFM images of unaged (a) and UV aged-336 h (b) Vectran™ HT fiber. Reproduced with permission.[77] Copyright 2013, Elsevier. [Color figure can be viewed at wileyonlinelibrary.com]

degradation of PBI, they exposed the PBI film at 350°C for up to 35 h using an environmental chamber that was continuously purged with dry air. To enable real-time film monitoring, the chamber was directly attached to an FTIR spectrometer, and infrared spectra of the specimens were acquired every 30 min. After the aging process, they found a slight color change (pale yellow to amber) in the PBI film and measured a weight loss between 3 and 5%. They observed that some FTIR peaks' intensity initially decreased with aging time. The researchers also reported the appearance of new peaks in the aged specimen. Among the newly formed peaks, one peak was found at 2222 $cm^{-1}$ and assigned to the aromatic nitrile group. Two other peaks were found in the region of 1500–2000 $cm^{-1}$: a peak at 1655 $cm^{-1}$ was assigned to a quinone structure of type 1, which is a conjugated ketonic structure, and a peak at 1713 $cm^{-1}$ suggested the presence of aliphatic ketones, although they noted that it was very unlikely considering the chemical structure of PBI. The researchers concluded that, throughout the PBI aging, the concentration of N-H groups steadily and continually declined. They also suggested that the oxidative attack caused the breakage of imidazole rings in the PBI structure, which subsequently resulted in the emergence of aromatic nitrile groups. And the formation of some carboxylic and carbonyl groups led them to the tentative identification of quinone and dicarboxylic acid structures as the by-products of that degradation.

### 3.6 | Aging of liquid crystal polyester (LCP) fibers

The aging of LCP fibers (Figure 19) still lacks investigation as only a few pieces of literature have been found, and only for UV and hydrothermal aging. Liu et al.[76] studied the effect of accelerated UV aging on Vectran™ fibers which is the commercial name of LCP fibers. The researchers subjected Vectran™ HT fibers to a high-pressure mercury lamp (60 $MW/cm^2$ at 365 nm) in the UV A range for up to 186 h while the distance between the UV lamp and the sample was kept at 10 cm. They found a 42.75% loss in the Vectran™ fiber tensile strength after irradiation. Furthermore, morphological analysis revealed the presence of micro-voids on the fiber surface of the aged fibers (Figure 20). Chemical analysis using X-ray photoelectron spectroscopy (XPS) and carbon-nuclear magnetic resonance (C-NMR) pointed towards a chain scission process in the fiber surface layer that may explain the fiber's loss in strength after UV exposure.

In a follow-up study, Liu et al.[77] exposed the Vectran™ HT fiber to a Xenon lamp (0.75 $W/m^2$ at 340 nm) for up to

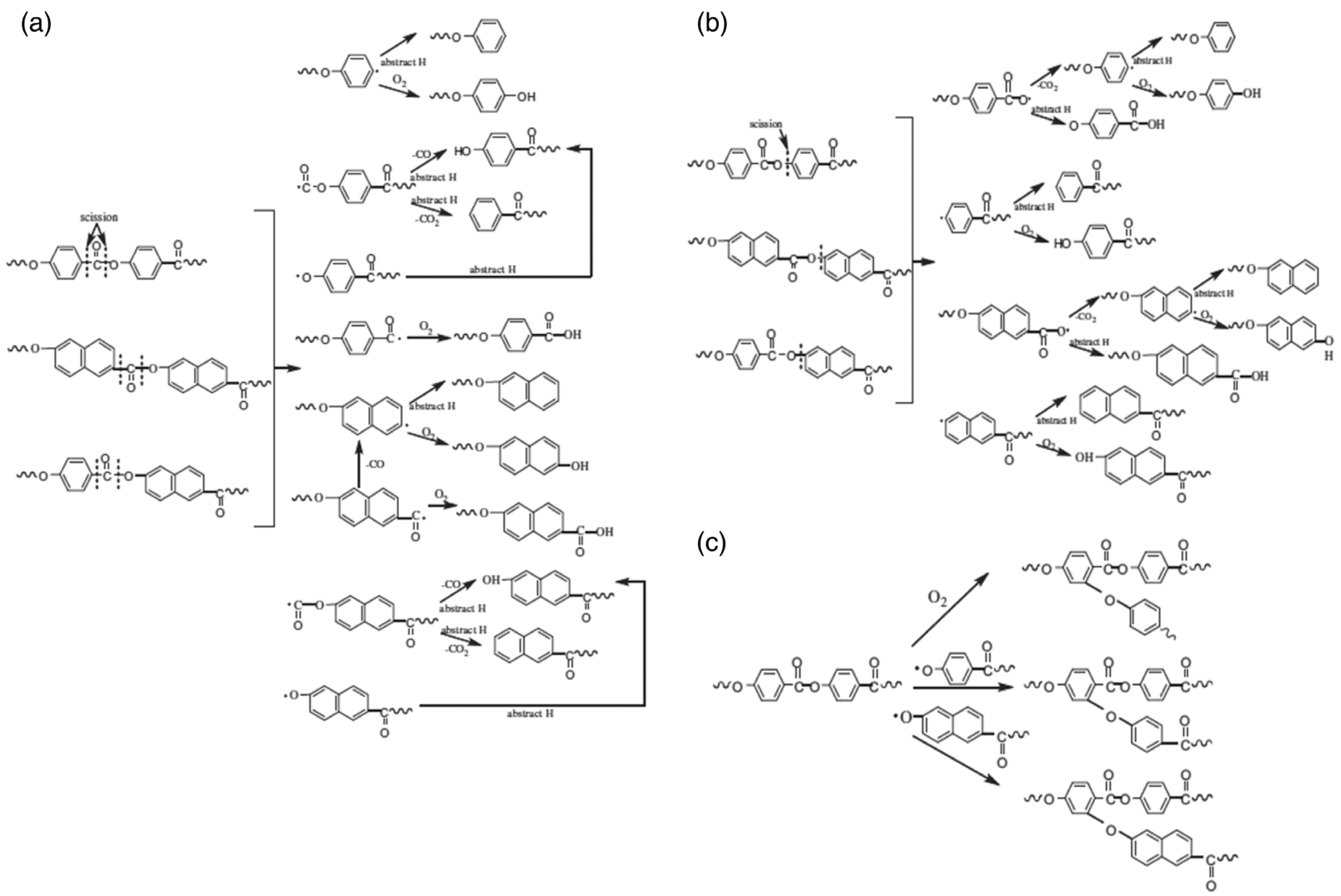

FIGURE 22 Three possible UV degradation mechanisms of Vectran™ HT fibers (identified as a, b & c). Reproduced with permission.[77] Copyright 2013, Elsevier.

336 h. The fiber's degradation accelerated with the increase in exposure time. The authors observed a 91% loss in the fiber's mechanical strength after the UV aging at 0.75 W/m$^2$ for 336 h. Furthermore, atomic force microscopy (AFM) analysis confirmed the morphological changes in the fiber as a result of UV aging (Figure 21). The researchers also reported a change in the crystal size (unaged: 5.07 nm, aged: 3.90 nm) and degree of crystallinity (unaged: 37.33%, aged: 36.95%) of the fiber due to UV irradiation for 336 h. They proposed a possible UV degradation mechanism of the Vectran™ HT fibers that involved the rupture of C-C bonds and C-O bonds in the aromatic polyester structure due to UV aging (Figure 22). This chain scission process can either abstract a hydrogen atom or react with oxygen, forming hydroxyl end groups.

In another study, Abu Obaid et al.[78] investigated the effect of hydrothermal aging on Vectran™ HT fibers. The researchers immersed fibers into water at 40, 60, 80 and 100°C for 30 consecutive days. They measured a 12% reduction in tensile strength of the fibers after aging for 30 days at 100°C. Because of the strong resistance of the LCP molecule to hydrolysis, the authors hypothesized that the 12% reduction in tensile strength was due to a slight disturbance such as chain slippage in the fiber structure. The authors did not observe any chemical change through FTIR either. On the other hand, two research works reported internal structural changes in Vectran™ fibers accompanied by an increase in the mechanical properties after exposure to thermal conditions.[79,80]

## 4 | FACTORS AFFECTING THE AGING OF THE HIGH-PERFORMANCE FIBERS USED IN FIREFIGHTERS' PROTECTIVE CLOTHING

### 4.1 | Exposure to high temperature and heat flux

As the occupation of a firefighter involves a high possibility of exposure to extreme temperature and heat fluxes, researchers have analyzed the effect of various exposure conditions such as the temperature, exposure duration, frequency of exposure, and the intensity of heat on firefighters' protective clothing residual performance. A

**TABLE 2** Summary of research work on the effect of high temperature and heat flux on firefighter clothing's performance.

| Reference | Sample fabric | Exposure condition | Exposure time | Parameter studied | Key findings |
|---|---|---|---|---|---|
| 81 | • Single layer (outer shell only), three-layers (outer shell + moisture barrier + thermal liner) clothing assembly.<br>• Fiber blend of the outer shell: Para-aramid, meta-aramid, PBI<br>• Fiber blend of the moisture barrier's textile component: para-aramid/meta-aramid/PBI<br>• Fiber blend of the thermal liner: Aramid/FR Cotton/Polyamide | • 10, 15, and 20 kW/m$^2$ radiant heat flux in combination with moisture.<br>• Water was sprayed until the sample's moisture content reached 20, 50, and 100%. | • Five minutes. | • Tensile strength. | • The synergistic effect of heat flux and moisture negatively affected the firefighters' clothing assembly.<br>• The effect of moisture was stronger on the three-layered assembly than on the outer shell only. |
| 72 | • Fire-protective fabrics typically used in the outer shell of firefighters' turnout gear. These fabrics were made from a different blends of para-aramid, meta-aramid, PBI, PBO, and LCP fibers. | • Fabric specimens subjected to 235°C in an air circulating oven | • 42 h | • Tear strength | • One fabric (para-aramid/PBI/LCP) exhibited an increase (11%) in tear strength, whereas all other fabrics encountered a very high reduction (25%–90%) in tear strength due to thermal exposure. |
| 82 | • Para-aramid/PBI blended plain weave outer shell fabric<br>• Polyimide/Para-aramid blended twill weave outer shell fabric. | • 30, 40, 50 and 60 kW/m$^2$ radiant heat flux applied to the outer shell fabrics combined with a moisture barrier and thermal liner | • Between 9 and 27 s at 30 kW/m$^2$, between 7 and 25 s at 40 kW/m$^2$, between 2 and 20 s at 50 kW/m$^2$, and between 1 and 15 s at 60 kW/m$^2$. | • Fabrics thermal stability<br>• Morphological changes<br>• Tensile strength. | • Evidence of fiber damage was found by SEM even when the specimens were only subjected to 30 kW/m$^2$ radiant heat flux.<br>• In some cases, a temporarily increase of tensile strength was measured after the thermal exposure. Ultimately, the tensile strength reduced considerably. |
| 83,84 | • Three para-aramid/PBI fibers blended outer shell fabrics. Two of the fabrics had a rip stop weave structure whereas another fabric was a twill weave with filament yarns in it. | • 10–70 kW/m$^2$ radiant heat flux. | • 30–300 s. | • Tensile strength. | • Exposure to a heat flux of 10–15 kW/m$^2$ only reduced by 5% the specimens' tensile strength.<br>• After a 300 second exposure to 20–30 kW/m$^2$, the specimens that were made with the rip stop weave structure exhibited a high tensile strength loss |

**TABLE 2** (Continued)

| Reference | Sample fabric | Exposure condition | Exposure time | Parameter studied | Key findings |
|---|---|---|---|---|---|
| | | | | | (26–32%), while a small strength loss (8%) was found for the fabric that was made from a twill weave structure.<br>• A 70 kW/m$^2$ exposure for 60 s reduced all three types of fabric specimens' tensile strength to 0. |
| 85 | • Two single layer coveralls made from para-aramid/PBI blended plain weave and meta-aramid/para-aramid/antistatic fiber blended plain weave fabrics. | • Full scale flame manikin test at 84 ± 2 kW/m$^2$ | • Four seconds | • Fabric thickness and mass<br>• Tensile and tear strength. | • The thickness of the specimens increased due to heat exposure.<br>• The thickness increase was larger for the meta-aramid/para-aramid/antistatic (82% with large standard deviations) than for the para-aramid/PBI fiber blended specimens.<br>• The mass loss was larger for the meta-aramid/para-aramid/antistatic fiber blended specimens (50%) than the para-aramid/PBI fiber blended specimens (8.2%).<br>• The tensile strength of both coveralls decreased after heat exposure. However, the para-aramid/PBI fiber blended specimens showed better tensile strength retention (average decrease of 39.5%) than the meta-aramid/para-aramid/antistatic fiber blended specimens (average decrease of 59.7%).<br>• Tear strength was also reduced in both thermally exposed fabrics. The average decrease in fabrics' tear strength was 70.2% for para-aramid/PBI fiber blended fabrics, whereas |

(Continues)

TABLE 2 (Continued)

| Reference | Sample fabric | Exposure condition | Exposure time | Parameter studied | Key findings |
|---|---|---|---|---|---|
| | | | | | meta-aramid dominated fiber-based fabrics lost on average 80.7% of their tear strength. |
| 59 | • Seven fire-protective fabrics typically used as outer shell in firefighters' turnout gear.<br>• The fabrics were made from different blends of para-aramid, meta-aramid, PBI, PBO, Basofil and carbon fibers. | • The fabric specimens were subjected to 150, 190, 210, 235 and 300°C using an air circulating oven | • Between one and 500 h. | • Tear strength<br>• Morphological analysis<br>• FTIR | • The fabrics' tear strength was significantly reduced (15%–33%) even after exposure at 150°C.<br>• The activation energy extracted from the tear strength data was between 81 and 113 kJ/mol depending on the fabric blend. The lowest activation energy (81 ± 9 kJ/mol) was reported for fabrics made from 100% meta-aramid fibers, whereas the highest activation energy (113 ± 7 kJ/mol) was reported for the fabric made from the para-aramid/PBI fibers blend.<br>• There was no discernible difference in the fiber microstructure between the unaged and thermally aged fibers.<br>• No evidence of chemical changes was observed by FTIR analysis |
| 86 | • Four fabric samples: Nomex IIIA, polysulfonamide (PSA), PBI/Kevlar and FR cotton. | • Repeated heat flux exposure of 84 kW/$m^2$ from a combined radiant and flame heat source. | • 3 s repeatedly for both bench scale and mannequin test | • Physical properties like fabric weight, thickness, dimensions, tear, and tensile strength.<br>• TPP. | • Repeated heat exposure deteriorated the mechanical and thermal protective performance of specimens. |
| 56 | • X-fiper® fabric (93% X-fiper® meta-aramid /5% para-aramid /2% antistatic fiber (P-140)). | • Heat flux of 6.5 and 9.7 kW/$m^2$. | • Exposure duration between 5 and 30 min. | • Mechanical properties like tear and tensile strength, elongation at break.<br>• TPP.<br>• Surface morphology of samples | • The mechanical properties (tensile strength, tear strength and elongation at break) decreased with the increase in exposure time and heat flux intensity. |

TABLE 2 (Continued)

| Reference | Sample fabric | Exposure condition | Exposure time | Parameter studied | Key findings |
|---|---|---|---|---|---|
| | | | | | • The TPP did not change significantly.<br>• Heat exposure caused grooves, peel-offs and deposits on the surface of the fibers. |
| 40 | • Fabrics made from 100% Kevlar, 100% Nomex, and combination of these constructed in a plain weave structure. | • Exposed to a temperature of 220°C and 300°C. | • Exposure time between 24 and 720 h. | • Weight.<br>• Tensile strength. | • The weight loss of the fabrics increased with the increase in temperature.<br>• The extent of the weight loss differed depending on the fiber content.<br>• The weight loss was higher for 100% Kelvar fabric specimens compared to other fabric specimens at 220°C for all exposure times (48, 240, 480 and 720 h).<br>• The presence of Nomex decreased the weight loss in the samples.<br>• The effect on tensile strength depended on the type of fabric, the temperature and the exposure time. |
| 62 | • Single-layered Nomex IIIA outer shell fabrics (93% Nomex/5%Kevlar/2% carbon fibers) of four different colors-blue, red, dark blue and yellow. | • Exposed to an incident heat flux of 10, 20, 30, 40 kW/m$^2$ in a cone calorimeter as well as multiple exposures at 20 kW/m$^2$. | • Exposure times between 10 and 2600 s. | • Tensile strength. | • After exposure to 20 KW/m$^2$ heat flux, the performance of the outer shell fabric changed considerably and a deterioration in the tensile strength was reported.<br>• The outer shell fabric color did not affect the degradation of fabric. |
| 87 | • A moisture barrier (e-PTFE membrane on a Nomex® fabric) that is typically used in firefighters' protective clothing. | • Five different temperatures between 190°C and 320°C applied with an air oven | • Exposure duration spanning from 1 to 1056 h | • Tensile strength<br>• Tear strength<br>• Water vapor permeability<br>• Surface morphology | • The moisture barrier specimens experienced a reduction in both tensile and tear strength with an increase in aging temperature and time. |

(Continues)

TABLE 2 (Continued)

| Reference | Sample fabric | Exposure condition | Exposure time | Parameter studied | Key findings |
|---|---|---|---|---|---|
| | | | | | • Significant reduction in the water vapor permeability (30% retention) when aged at 190°C for 24 days.<br>• SEM images revealed the occurrences of pore closure in the ePTFE membrane aged at the lowest temperatures. It also showed cracks and holes in the specimens when aged at 275, 300 and 320°C.<br>• The authors reported that there was no visual indication of material degradation in the aged specimens by the naked eye. |
| 38,39 | • Fabric from a blend of 60% Kevlar and 40% PBI staple fibers. | • Exposure to temperatures between 190°C and 320°C. | • Exposure duration spanning from less than an hour to two weeks. | • Tensile strength.<br>• Chemical changes (FTIR). | • The tensile strength of the fabric and of yarns extracted from aged specimens reduced as a result of accelerated aging.<br>• The degradation of the fabric occurred for an exposure to a temperature as low as 190°C.<br>• The chemical structure of the fibers was only slightly modified as a result of thermal exposure. |
| 29 | • Six different fabric assemblies were examined.<br>• The outer shell of these fabrics was made from individual or blend of aramids, PBI and Basofil fibers. | • Exposed to a heat flux of 40 $kW/m^2$ for radiant heat and 80 $kW/m^2$ for convective heat. | • Exposure duration spanning from 17 to 33 s. | • Tensile and tear strength. | • The heat protection performance of the samples reduced after heat exposure. However, the values remained above the requirement of the standard (EN 469:2005) for firefighters' protective clothing.<br>• The degradation of the fabrics started before a visual change, that is, discoloration of fabric, occurred. |

summary of a series of research works is given in Table 2. The table identifies the sample type and fiber content, the exposure condition and duration, and the parameters studied. It also provides the key findings.

As it can be observed in Table 2, researchers used different types of protocols for assessing the thermal aging behavior of firefighters' protective clothing. These procedures can be grouped into two categories. The first category corresponds to the aging of fabrics through convective thermal exposure. The second category involves the aging of fabrics through radiative thermal exposure. For instance, Arrieta et al.[38,39]; Dolez et al.[59]; Ozgen & Pamuk[40]; Yehia[72] and Aidani et al.[87] investigated the thermal aging of fire-protective fabrics by subjecting fabric specimens to elevated temperatures (between 150 and 320°C) using an air circulating oven. On the other hand, Cui et al.[56]; Deng et al.[85]; Fulton[83]; Liu et al.[82]; Mazumder et al.[81]; Ohalele et al.[84]; Rezazadeh[62]; Rossi et al.[29]; and Wang & Li[86] assessed the thermal aging of fire-protective fabrics by exposing fabric specimens to heat fluxes between 6.5 and 84 kW/m$^2$ using a cone calorimeter or a flash fire manikin. An important difference between the two types of thermal aging protocols lies in the exposure time. Researchers who applied convective thermal aging with an oven used much longer thermal exposure times (between one and 720 h) compared to researchers who used radiative thermal exposure with a cone calorimeter or a flash fire manikin (between 1 and 2600 s). As the degradation processes may not be the same,[38] a question can be raised about the significance of the results of short exposures to high radiative heat fluxes for the long-term aging of fire-protective fabrics experienced in the field.

Table 2 also shows that, regardless of the exposure protocol, thermal aging highly affects the strength of fire-protective fabrics made from high-performance fibers. For instance, even at 150°C exposure (in convective heat), fire-protective fabrics made from different blends of high-performance fibers (para-aramid, meta-aramid, PBO, Basofil, PBI) exhibited a significant decrease in their tearing strength.[59] The researchers reported more than 60% loss in the tearing strength of 100% para-aramid fiber-based fabric after exposing it to 150°C for 500 h. This high tear strength reduction in para-aramid fiber-based fabric specimens at 150°C is surprising as 150°C is lower than the continuous operating temperature (190°C) reported for para-aramid fibers.[11] In another study, Cui et al.[56] reported a 24% decrease in the tensile strength of a fabric made of 93% meta-aramid/5% para-aramid/2% P-140 when subjected to radiative heat fluxes of 9.7 kW/m$^2$ for 30 min. In all instances, the deterioration of fabrics' strength increased with the increase of thermal exposure intensity and duration.

Researchers have also reported the negative effect of thermal aging on fabric thickness,[85,86,88] mass,[40,85,86,88] and dimensions.[86] Regarding chemical changes, Arrieta et al.[38] did not find large differences between unaged and thermally aged (at 275°C for 191 h) para-aramid/PBI fibers blended fabrics by FTIR analysis. On the other hand, they showed changes in the fiber crystallinity by X-ray diffraction and Raman spectroscopy as a result of thermal aging.[39]

Finally, contradictory results were found on the effect of thermal exposure on the TPP of high-performance fiber-based fire-protective fabrics and on fiber morphology. For instance, Cui et al.[56] did not find any change in the TPP of a fire-protective fabric (93% X-fiper®/5% para-aramid/2% P-140) after subjecting it to 9.7 kW/m$^2$ for 30 min. On the other hand, Wang & Li[86] found a negative effect on the TPP of a fire-protective fabric (93% meta-aramid/5% para-aramid/2% P-140) after subjecting it to 84 kW/m$^2$ for 3 s. Since both fabrics had a similar fiber content, it is possible that the intensity of heat flux actually caused the difference in behavior observed between the two studies. Regarding the fiber morphology, Cui et al.[56] and Liu et al.[82] reported evidence of fiber damage due to thermal aging after subjecting fabric specimens to 30 kW/m$^2$ for 27 s and to 6.5 kW/m$^2$ for 300 s. On the contray, Dolez et al.[59] did not find any evidence of fiber damage after exposing fabric specimens to 300°C for 100 h. However, the research by Dolez et al.[59] subjected fabric specimens to thermal aging using an air-circulating oven whereas Cui et al.[56] and Liu et al.[82] used a cone calorimeter. This apparent discrepency may point towards differences in degradation mechanisms between long term exposure to convective heat and short term exposure to radiant heat. It may be noted that, in these three studies, the effect of heat exposure on the mechanical performance was severe.

## 4.2 | Exposure to ultraviolet radiation

During firefighting activities, firefighters, in particular wildland firefighters, may be exposed to large amount of sunlight.[89] Firefighters' clothing may also be exposed to UV radiation during storage. As a result, researchers have studied the effect of UV radiation and sunlight on fire protective fabrics and firefighters' protective clothing. A summary of existing research regarding the effect of long-term exposure to UV radiation is given in Table 3.

As can be seen in Table 3, researchers covered a wide range of irradiances (between 0.24 and 1.55 W/m$^2$), temperatures (between 40 and 80°C), and RH (between 29 and 50%) when assessing the UV aging behavior of firefighters' protective clothing.[41,44,45,51,57,58,60,83,90–92] There is a strong agreement among all the articles regarding the reduction

**TABLE 3** Summary of research work on the effect of long-term exposure to UV radiation and sun light on firefighter clothing's performance.

| Reference | Sample fabric | Exposure condition | Exposure time | Parameter studied | Key findings |
|---|---|---|---|---|---|
| 90 | • Two outer shell fabrics. One fabric (Outer shell I) was made from 70% meta-aramid, 23% Lenzing FR, 5% Twaron, 2% Beltron fibers with a rip stop structure. The other fabric (Outer shell II) had a twill weave structure and was made of 79% Proban, 20% polyester and 1% antistatic fibers. | • The outer shell fabric specimens were exposed to fluorescent UV light using a weathering machine.<br>• The irradiance intensity was 0.89 $W/m^2/nm$ (at 340 nm) | • 13 days | • Tensile strength.<br>• Air permeability.<br>• Bending moment.<br>• Water vapor resistance. | • UV aging caused a 13.1% reduction in tensile strength for Outer shell I. Outer shell II experienced a 9.7% loss in tensile strength due to UV aging.<br>• Air permeability for both specimens was reduced after UV exposure. Outer shell I experienced a 15.8% reduction in air permeability whereas Outer shell II had a 9.7% reduction.<br>• The fabrics' bending moment was negligibly affected (9.8% decline for Outer shell I and 6.9% for Outer shell II) due to UV exposure.<br>• Water vapor resistance increased by 10% for Outer shell I and 12.5% for Outer shell II. |
| 91 | • Nine fire-protective fabrics made from different blend ratios of para-aramid and meta-aramid fibers<br>• All the fabrics had rip stop weave structure<br>• Three fabrics had water repellent finishes. | • Fabric specimens were exposed to UV light by using a xenon-arc weathering chamber.<br>• The lamp had the radiation intensity of 180 $W/m^2$<br>• Fabric specimens were exposed between 34 and 340 $MJ/m^2$ over a 300–400 nm wavelength range.<br>• Black panel temperature was 63°C and relative humidity was 50% | • Between 52.4 and 524 h. | • Tensile strength. | • The tensile strength of all fabrics declined significantly due to UV aging.<br>• Having a water repellent finish did not increase the UV resistance of the fire-protective fabrics. |
| 92 | • Four knitted fabric samples used in firefighters' protective hoods. | • The fabric specimens were exposed to UV light | • Between 30 and 120 h. | • Bursting strength.<br>• Color change<br>• TPP. | • All four fabrics exhibited a decline in bursting strength due to UV exposure. |

TABLE 3 (Continued)

| Reference | Sample fabric | Exposure condition | Exposure time | Parameter studied | Key findings |
|---|---|---|---|---|---|
| | • All the knitted fabrics had a 1 × 1 rib structure made from different blends of meta-aramid, PBI, FR rayon, oxidized PAN and artificial tri blend fibers. | by using a Xenon arc weather-ometer. • The irradiance was 0.55 W/m$^2$ (at 340 nm). • The weather-ometer chamber temperature was 62 ± 2°C. | | • Particulate filtration efficiency (PFE). | • The 100% meta-aramid fabric experienced a sharp decrease in bursting strength, whereas the other fabrics made from 20% meta-aramid/80 FR rayon, and 20% PBI/80% FR rayon experienced a comparatively slighter decrease. • The fabric made from 65% oxidized PAN/35% artificial tri-blend experienced the highest loss in bursting strength. • Color changes were visible in the UV-aged specimens. • The TPP of the specimens was not affected by UV exposure. • The PFE of the specimens did not change due to UV aging. |
| 51 | • One outer shell fabric is a blend of Kevlar/ PBI (40/60) with a twill constructed rip-stop weave structure. • The other woven fabric is a Nomex-IIIA (Nomex/ Kevlar/ antistatic; 93/5/2) • Both fabrics had the same weight per unit area (220 g/m$^2$). | • The samples were exposed to a UV irradiation of 0.24 ± 0.01 W/m$^2$ (at 340 nm) at 40°C and 50% RH in a weather-o-meter equipped with a Xenon lamp. | • Four days | • Tensile and tear strength • Thermal performance properties | • Strength loss was observed in the UV aged specimens. • Exposure to heat accelerated the degradation of the PBI fiber-containing fabrics. |
| 83 | • Three 60% para-aramid/40% PBI fibers outer shell fabrics. Two of the fabrics had a rip stop weave structure whereas the other fabric had a twill weave structure with filament yarns in it. | • The specimens were exposed to UV light using a Xenon lamp weather-o-meter. • The irradiance intensity was 1.1 W/ m$^2$ at 420 nm. • The black panel temperature was approximately 66–70°C. | • Between 40 and 160 h | • Tensile strength • Near-infrared (NIR) spectroscopy spectra. • Morphological analysis | • All three fabrics exhibited a decrease in tensile strength due to UV aging. • The fabric made with a twill weave structure had the best tensile strength retention (71%) after 160 h of UV aging compared to 51 and |

(Continues)

TABLE 3 (Continued)

| Reference | Sample fabric | Exposure condition | Exposure time | Parameter studied | Key findings |
|---|---|---|---|---|---|
| | | • The RH was approximately 29–34%. | | | 60% for the two rip stop fabrics.<br>• Both fabrics made of the rip stop structures showed an increase in reflectance after UV exposure. On the contrary, the reflectance decreased for the twill weave fabric. However, these changes in reflectance were only limited.<br>• Fiber damage was evident even after 40 h of UV aging. |
| 60 | • Outer shell fabrics with a rip-stop weave structure made from different blends of meta-aramid, para-aramid, and PBI fibers. | • Accelerated exposure to UV irradiance through a Xenon lamp system. Fabric specimens were exposed to 0.24 ± 0.01 $W/m^2$ (at 340 nm wavelength) while the temperature and RH of the UV chamber were 40°C and 50%, respectively. | • The fabric specimens were exposed for a duration between 1 and 7 days. | • Mechanical properties of fabrics (tensile strength, tear strength, abrasion resistance, elongation at break).<br>• Surface and chemical analysis of specimens by SEM, FTIR, TGA. | • The mechanical properties of the fabrics were negatively affected by UV exposure.<br>• Even short durations (1 day) deteriorated the mechanical properties of the fabric specimens.<br>• In the case of meta-aramid fiber-based fabrics, the mechanical properties of the samples were reduced more strongly than for the para-aramid and PBI blended fiber-based fabrics.<br>• FTIR and TGA results hint at a possible aramid cleavage followed by chain cleavage, which could be a reason for the sample's mechanical performance loss.<br>• SEM analysis showed that after the UV exposure, the fiber surface deteriorated, decomposed, and became rough. |

**TABLE 3** (Continued)

| Reference | Sample fabric | Exposure condition | Exposure time | Parameter studied | Key findings |
|---|---|---|---|---|---|
| | | | | | • The abrasion resistance decreased after UV exposure performance, especially for the meta-aramid fabric specimens. |
| 64 | • A moisture barrier (e-PTFE/Nomex®) that is typically used in firefighters' protective clothing. | • The specimens were exposed to four UV irradiances (0.35, 0.68, 1.00, 1.35 W/$m^2$) at 50, 70 and 80°C. The irradiance was measured at 340 nm. | • 360 h | • Tensile and tear strength<br>• Water vapor permeability<br>• Surface morphology (SEM, AFM)<br>• Chemical analysis (FTIR, XRD, DSC). | • Significant deterioration in the moisture barrier's tensile and tear strength, upon UV aging, worsening with the more severe aging conditions.<br>• The water vapor permeability was reduced by 25% for the specimens aged at 1.35 W/$m^2$ for 250 h.<br>• DSC revealed a deterioration of the material's glass transition temperature due to UV aging.<br>• A synergistic effect of temperature and UV radiations was mentioned by the authors.<br>• SEM imaging revealed the presence of cracks, holes and deterioration in the fiber morphology while aged at 1.35 W/$m^2$ irradiance.<br>• A peak (1725 $cm^{-1}$) was found on aged specimens that pointed towards the formation of carboxylic acid during the photo-oxidation of the e-PTFE membrane.<br>• The authors found an increase in the Nomex® fibers' crystallinity with the increase in aging time. |

(Continues)

TABLE 3 (Continued)

| Reference | Sample fabric | Exposure condition | Exposure time | Parameter studied | Key findings |
|---|---|---|---|---|---|
| 57 | • Two outer shell fabrics<br>• PBI/Para-aramid (40/60) blended woven fabric with rip-stop weave structure<br>• Meta-aramid/Para-aramid/Antistatic fiber (93/5/2) blended woven fabric with plain weave structure | • A sphere-based (mercury arc lamp) weathering device was used for continuous UV exposure to fabric specimens at 15.9 ± 0.02 kJ/m$^2$ while the temperature and RH of the UV chamber were 50 ± 0.1°C and 50 ± 1%, respectively. | • The fabric specimens were exposed for a duration between 1 and 66 days. The researchers converted these accelerated UV exposure conditions to the simulated exposure time under the continuous sun, natural conditions, and turnout gear conditions. According to their conversion, the accelerated aging treatment applied corresponded to a continuous sun exposure between 7.4 and 488 days, natural weathering conditions between 19.7 and 1300 days, and turnout gear use conditions between 0.5 and 32 years | • Tear strength on fabric specimens.<br>• Tensile strength on yarn specimens.<br>• Microscopic analysis<br>• Chemical analysis by ATR-FTIR. | • The meta-aramid fiber dominant fabric specimens were more affected by UV irradiation than the para-aramid/PBI fibers blended fabric specimens. The meta-aramid fiber dominant fabric experienced a 43% decrease in tear strength after one day of UV exposure, and 73% after 2.6 days of exposure. By comparison, the decrease in tear strength for the para-aramid/PBI blended fabric specimens was 54% after six days of UV exposure. The same trend was observed for the yarn tensile strength.<br>• A change in the fiber surface morphology was reported for both fabrics.<br>• ATR-FTIR analysis showed evidence of amide linkage cleavage due to UV aging of aramid fibers. |
| 44 | • Four outer shell fabrics were used. Three fabrics were a blend of melamine/para-aramid (40/60) fibers with differences in fabric characteristics like thickness, weight, and water repellent finishes. Another fabric was a blend of melamine/para-aramid/PBO (32/60/8) fibers. | • The fabric specimens were subjected to 15.9 ± 0.02 kJ/m$^2$ while the temperature and RH of the UV chamber were 50.0 ± 0.1°C and 50 ± 1%, respectively. | • The fabric specimens were exposed for durations between 1 and 28 days, which was estimated by the researchers to correspond to continuous sun exposure between 7.4 and 207 days, natural weathering conditions between 19.7 and 552 days, and turnout gear use conditions between 0.5 and 13.6 years. | • Tear strength on fabric specimens.<br>• Tensile strength of yarns.<br>• Thermal protective performance (TPP). | • All the fabrics experienced a loss in mechanical performance due to UV aging. The melamine/para-aramid fabric that did not have a water-repellent finish encountered the highest UV degradation with 93% loss in tear strength after 28 days of UV exposure. The fabric that was dyed with |

**TABLE 3** (Continued)

| Reference | Sample fabric | Exposure condition | Exposure time | Parameter studied | Key findings |
|---|---|---|---|---|---|
| | | | | | black color showed the highest resistance to UV aging (62% loss in tear strength after 28 days of UV irradiance). The results of yarn tensile strength echoed the fabric tear strength behavior.<br>• The TPP was reduced after UV aging but still met the minimum requirement of NFPA. |
| 41 | • Outer shell fabric made from a blend of Kevlar/PBI (60/40) fibers. | • Specimens were exposed to several UV irradiances spanning from 0.35 to 1.55 W/m$^2$ for four different temperatures: 50, 60, 70, and 80°C. | • Specimens were exposed for a duration of 4 to 15 days. | • Mechanical properties (breaking force) tested on yarns extracted from the aged fabric specimens.<br>• Chemical analysis by ATR-FTIR. | • The yarn breaking force decreased with the exposure duration.<br>• The deterioration in strength was attributed to a photo-oxidative reaction. |
| 45 | • The sample was a Twaron2000 fiber (para-aramid). | • The specimens were exposed to UV emitted by a carbon arc lamp in a UV Auto Fade Meter U48 AU chamber at 40°C temperature and 45% RH. | • The specimens were subjected to UV for up to 144 h. | • Mechanical properties (tear and tensile strength of the fiber).<br>• Chemical analysis by SEM, XRD, DSC, DMA and ATR-FTIR. | • UV exposure decreased the mechanical properties of the fiber.<br>• Morphological changes were observed on the fiber surface.<br>• The crystallinity did not change but some rearrangements occurred in the crystalline areas, which was associated with the surface etching and caused the strength loss of the fiber. |
| 93 | • Five fabrics commonly used as outer shell of firefighters' protective clothing: Nomex III, Polyamide/FR viscose blend, Proban FR cotton, | • The samples were exposed to a 6500-Watt xenon arc Weather-O-meter. The UV irradiance was 0.75 ± 0.02 W/m$^2$ and the RH was 35 ± 5% while the black panel | • All the samples were exposed for 40 h. | • Color<br>• Tear strength,<br>• Flame resistance<br>• TPP | • Among the five fabrics, Nomex III, Zirpro FR wool, and PBI/Kevlar were vulnerable to light and significantly decreased in tensile strength. |

(Continues)

TABLE 3 (Continued)

| Reference | Sample fabric | Exposure condition | Exposure time | Parameter studied | Key findings |
|---|---|---|---|---|---|
| | Zirpro FR wool, and PBI/para-aramid (40/60). | temperature of the O-meter was 60 ± 2°C and the silver panel temperature was 42 ± 2°C. | | | • Color changes happened to all the samples which contained aramids.<br>• The TPP of whole clothing assemblies did not change much due to UV exposure. |

in tensile strength of fabrics used in firefighters' protective clothing due to UV aging. Even fabric specimens subjected to a lower irradiance intensity like 0.24 W/m$^2$ for four days experienced a significant degradation (more than 60% reduction in tensile strength).[51]

Apart from the negative effect on fire-protective fabrics' tensile strength, researchers also reported color changes,[58,83] fiber surface damage[45,57,83] and chemical modifications[41,57,60] as a result of UV aging. On the other hand, researchers did not find a considerable effect on the TPP of fabric specimens after exposure to different UV conditions.[44,58,92]

## 4.3 | Exposure to abrasion

Firefighting involves demanding physical activity, such as crawling.[89] Also, during firefighting operations, firefighters and their protective clothing come in direct contact with the fire ground and the fire-fighting equipment. These situations cause a high level of abrasion in the firefighters' protective clothing. The result of this abrasion may involve the formation of micro-cracks in the fibers, followed by deeper cracks leading the fiber and fabric towards mechanical degradation.[94]

Only a limited number of research articles have been found on the effect of abrasion on high-performance fiber-based firefighters' protective clothing. Nazaré et al.[44] examined the abrasion resistance of four fire-protective fabrics made from different blends of melamine, para-aramid, and PBO fibers. Using a Martindale abrasion tester and standard wool fabric as the abradant, the fabric specimens were subjected to up to 20,000 rub cycles. Following the 20,000 cycles, none of the specimens exhibited any evidences of rupture, revealing the excellent abrasion resistance of those fire-protective fabrics. In another study, Pang et al.[95] investigated the abrasion resistance of fire-protective fabrics made from basalt fibers with three different weave structures - plain, twill, and weft satin. The fabric specimens were subject to up to 200 abrasion cycles using a rotary fabric abrasion testing equipment. They reported a slight weight loss in the plain weave (0.23%) and twill weave (0.73%) fabrics. A comparatively higher weight loss (4.69%) was reported for the satin weave fabric. The loose structure of the satin weave was identified as the cause of this weight loss of the fire-resistant fabric after repeated abrasion cycles.

## 4.4 | Exposure to moisture

Firefighters are also exposed to water from weather and the fire-extinguishing medium.[89] Besides, the clothing wearer's perspiration may also contribute to the fabric's moisture content.[96–98] Engelbrecht-Wiggans et al.[53] reported a 14% reduction in para-aramid yarn's tensile strength after aging at 76% RH and 70°C for one year. They did not observe any chemical changes in the aged fibers by ATR-FTIR. Li et al.[99] investigated the structure of para-aramid fibers after long-term exposure to different RH aging environments at temperatures between 60°C and 90°C. They did not find any evidence of changes in the crystal structure of the aged fibers. On the other hand, Arrieta et al.[41] showed a strong detrimental effect of hydrolytic aging conditions on a para-aramid/PBI blended fire-protective fabric. They observed a 50% decrease in the residual tensile strength of yarns collected from the aged fabric specimens when exposed to 60% relative humidity (RH) at 80°C for 31 days. The sensitivity of para-aramid fibers to hydrolysis was mentioned as a possible reason for the degradation of the fabrics' mechanical performance observed. The presence of PBI fibers in the blend and their high residual sulfur content was later identified as the culprit of this premature degradation observed in para-aramid/PBI blended fire-protective fabrics.[54] It leads to the acidification of the aqueous environment which acts as a catalyst for the hydrolysis of the para-aramid fibers.

Researchers have also found a negative impact of moisture aging on fabrics that contain PBO fibers. For instance, Chin et al.[24] exposed twenty-four woven PBO body armor panels to RH of 37% and 60% at temperatures of 50°C and 60°C for up to 157 days. Tensile strength tests performed on PBO yarns extracted from the aged fabrics revealed approximately 40% strength reduction due to aging. Additionally, FTIR analysis of aged samples showed that the benzoxazole ring opened in the PBO chemical structure, followed by the creation of carboxylic acid and aminophenol groups, which was connected to the hydrolysis of PBO. However, Hoque et al.[54] did not evidence a considerable effect of water on the mechanical performance of a PBO fiber-based fabric. They exposed a para-aramid/meta-aramid/PBO (40/20/20%) blended fire-protective fabric to hydrothermal aging conditions by water immersion at 60, 80, and 90°C for up to 1200 h. The residual tensile strength did not deteriorate significantly while aged at 60 and 80°C for 1200 h. A slight decrease (25%) was found in fabrics' tensile strength while aged at 90°C for 1200 h.

## 4.5 | Exposure to laundering

Cleaning is done on firefighters' protective clothing assembly to remove debris, soiling, and other contamination. The recent edition of NFPA 1851[100] describes three ways of cleaning firefighters' protective clothing. The first step is the primary exposure reduction by the user after every firefighting operation. This mild cleaning can be done through dry or wet mitigation techniques. Firefighters' turnout gear that is soiled or contaminated or at least twice a year goes through advanced cleaning. Training personnel completes advanced cleaning using mild detergent and water at 40°C. Specialized cleaning is the third way of cleaning, which is done by a specialized company with appropriate training and verification or an independent service provider (ISP), or any verified organization or cleaner.[100] Specialized cleaning is done for very specific types of soils or contaminants, or when advanced cleaning is not efficient at cleaning the firefighters' turnout gear.

A few studies have been conducted on the effect of laundering on firefighters' protective clothing. In one of them, seven fabrics corresponding to different fiber blends used in fire-protective clothing were subjected to up to 50 washing and drying cycles per the NFPA 1971 washing/drying sample preparation procedure.[55] The authors reported a reduction of up to 66% in the tear strength of the fabrics after 50 washing and drying cycles. This decrease in the fabrics' tear strength varied with their fiber content. They observed a high reduction in the tear strength of most fabrics containing a high percentage of para-aramid fibers, with the exception of a Kevlar/Nomex/PBO fabric. No significant changes were measured in meta-aramid-based fabrics. Makinen[101] investigated the thermal, mechanical, and comfort properties of four fabrics - aramid, FR cotton, FR wool, and FR viscose blend - after subjecting them to up to 50 laundering cycles. They reported an increase in the water absorption and a decrease in the air permeability of these four fabrics due to the repeated launderings. Nazaré et al.[44] subjected four fire-protective fabrics to five washing cycles followed by air drying. The four fabrics had the same 60% para-aramid / 40% melamine fiber content but different physical properties and surface chemical finishes. The authors reported a 20% reduction in the tear strength of one of the fabrics that did not have a surface finish, while the effect of the five washing cycles was minimal for the fabrics with a surface finish.

In the last revision of the NFPA 1851[100] standard, the frequency of cleanings has been increased to try reducing the risk of cancers among the firefighters. Since 2012, the World Health Organization has listed firefighting occupation as a potential risk for carcinogenic exposure.[102] The chemical or toxic gases firefighters are exposed to are considered as one of the potential reasons of their higher risk of cancers. The objective of this increase in the cleaning frequency of firefighters' bunker suits is to remove the toxic chemicals remaining in the fabrics of the turnout gear after the firefighting operation.[103] However, this increased frequency of cleaning could become a possible source of premature aging for the outer shell of firefighters' protective clothing.

## 4.6 | Exposure to combined conditions

In real scenarios, firefighters' protective clothing is exposed to a combination of different aging conditions present concurrently or alternatively. However, only a few studies used laboratory aging[104,105] or outdoor weathering[106–108] to examine the combined effect of aging conditions on protective clothing.

Dolez et al.[104] investigated the combined thermal, photochemical, and hydrolytic aging behavior of a moisture barrier used in firefighters' protective clothing. For that study, the researchers subjected e-PTFE/Nomex laminated moisture barrier specimens to alternating cycles of UV and 100% RH at two temperatures using a UV chamber equipped with UVA lamps. The cycles involved 4 h of UV at 0.68 W/m$^2$ (measured at 340 nm) and 4 h of 100% RH at 50 or 60°C. The authors reported a considerable decrease in the tearing strength of the aged specimens. They were able to describe the thermal life of the aged moisture barrier using the following equation[104]:

$$t_L = A \times I^{\propto} \exp\left(\frac{E_a}{RT}\right) \times \exp\left(C \times RH\right) \qquad (1)$$

In this equation, $t_L$ refers to the thermal life of the moisture barrier after exposure to the combined thermal, photochemical, and hydrolytic aging conditions. I indicates the UV intensity; T corresponds to the temperature in the chamber, and RH is the relative humidity. The researchers found a very good agreement between their model and the experimental data.

In another study, Vanderschaaf et al.[105] investigated the effect of the combined action of repeated abrasion and laundering on three fire-protective fabrics that are typically used in flame-resistant work wear. These three fabrics were made from different blends of cotton, nylon, modacrylic, Lyocell regenerated cellulose, para-aramid, meta-aramid, and anti-static fibers. The fabric specimens were abraded using a brush pilling tester according to a modified version of the ASTM D3511[109] test standard. The modification to the test method was made to increase the severity of the abrasion on the fabric specimens. The fabric specimens were laundered (for up to 25 cycles) between each series of 1-minute abrasion cycles. The researchers reported a significant reduction in the fabrics' tensile strength after combined abrasion and laundering: 57%, 24% and 22% loss of tensile strength in the cotton/nylon, meta-aramid/para-aramid/anti-static carbon, and modacrylic/lyocell/para-aramid fabrics, respectively, after 25 abrasion/laundry cycles. Apart from tensile strength, the researchers also noted changes in the specimen's mass, thickness, morphology, and color due to repeated abrasion and laundering. On the other hand, they did not find any significant changes in the fabrics' flame resistance and thermal protective performance.

Lion Apparel[108] investigated the effect of temperature, moisture, and natural light on the outer shell fabrics of firefighters' protective clothing. They selected South Florida and Central Arizona as the two natural weathering conditions for this project since those areas offer long daylight hours (8–10 h on average) and similar temperatures (37°C in Central Arizona and 30°C in South Florida during the experiment). On the other hand, the two regions are known to have opposite humidity patterns (dry for Central Arizona vs. humid for South Florida). The researchers reported that the fabric specimens lost between 30 and 75% of their tear strength after nine weeks of exposure to natural weathering. They noticed that the fabric specimens that were subjected to the weather of Central Arizona experienced a slightly higher degradation than those exposed to the South Florida area. However, the researchers could not identify the reason behind this slight difference in the degradation of the fabrics. Apart from that, they found that, in general, fabrics with a higher amount of para-aramid fibers (> 50%) exhibited a greater resistance to natural weathering than fabrics with a relatively low para-aramid fiber content. The researcher also noticed that the para-aramid fiber-dominated fabrics with dark shades (such as black) tended to be more resistant to sunlight than the same materials with lighter shades.

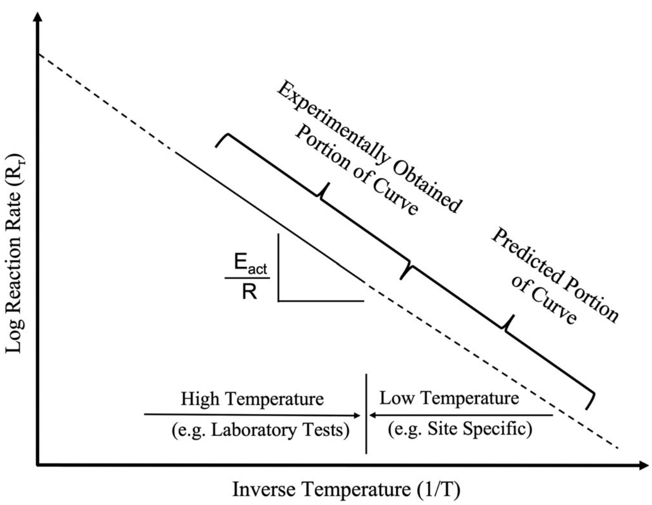


FIGURE 23 Schematic illustration of the Arrhenius plot. Reproduced with permission.[111] Copyright 1992, Elsevier.

In another research on outdoor weathering, Fries[107] subjected firefighters' turnout coats to natural weather using the facility at the Frauenhofer Institute (ISE) in Freiburg/Breisgau – Germany. They exposed the samples to natural weathering (at a 45° angle, facing south) for 14 days. They found that polyamide-imide fiber-based turnout coats lost more than 85% of their tear strength after 14 days of exposure. However, the researcher did not provide further reasons for their observation.

## 5 | MODELS FOR STUDYING THE AGING BEHAVIOR OF FIRE-PROTECTIVE FABRICS

Researchers have used accelerated aging conditions to characterize materials' aging behavior, including fire-protective fabrics, in the shortest possible time. The findings from the accelerated aging studies may include the degradation kinetics, a sign of any induction period, or a distinct stage in the material before it reaches the failure stage.[110] They have employed different strategies to use the data generated under these accelerated aging conditions to predict the long-term behavior of fire-protective fabrics in conditions relevant to service. The techniques most often encountered in the study of the aging behavior of fire-protective fabrics are the Arrhenius model and the Time–Temperature Superposition (TTS) principle. Recently the use of the Hill equation was proposed for the description of the kinetics of thermal aging of fire-protective fabrics.

### 5.1 | The Arrhenius model

The scientific community has realized for a long time the dependence of chemical reactions on temperature.[111,112] Even a slight increase in temperature may impact a chemical reaction rate immensely. The Arrhenius equation (Equation 2) describes the effect of the temperature on the rate of chemical reactions $R_r$.[110,113] $E_a$ denotes the activation energy of the reaction, R is the gas constant (8.314 J/mol.K), and T refers to the absolute temperature.

$$R_r = A \exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

The Arrhenius equation has been used to predict the service life of thermally aged textile materials made from polymers.[110] Generally, the textile aging experiment is performed at a high temperature for a shorter time. The chemical reaction rate at a lower temperature is predicted using the Arrhenius model, as shown in Figure 23.[111]

The Arrhenius model has successfully been used by researchers to describe the effect of thermal aging on the performance of fire-protective fabrics, for example, tensile strength[38] and tear strength.[59] In addition, it also satisfactorily depicted the contribution of temperature to the aging produced by other conditions, for example, UV[41] and moisture.[54] Finally, Equation 1 illustrates its application when temperature was used to accelerate the aging produced by UV and moisture subjected alternatively to the fabric specimens.[104]

However, in order to apply the Arrhenius equation for extrapolating experimental data, two assumptions are made.[110,114] The first assumption is to have a one chemical reaction across the aging process while the second assumption is to have identical activation energies for the range of temperatures used. It has been observed that these assumptions are not always met while studying polymer aging, leading for instance in a curvature in the Arrhenius plot.[115,116] The activation energy may not always be independent of the temperature, especially when the reaction involves more than one process.[110,117] In addition, a polymer may deviate from the Arrhenius behavior when the range of aging temperatures used cross the glass transition or the melting temperature of the polymer.[118]

## 5.2 | The time–temperature superposition principle

The time–temperature superposition (TTS) principle is commonly used in polymer science either to estimate a viscoelastic polymer's temperature dependency or to interpolate the length of time or frequency at a specific temperature at which the material's behavior has been studied.[119] The use of the TTS principle improves the accuracy of the extraction of polymers' activation energy and lifetime prediction.[113] According to the TTS principle, the material's property measured after exposing it for a short time to a higher temperature is equivalent to the material's property after being exposed to a lower temperature for a prolonged time. Following this principle, a shift factor ($a_T$)

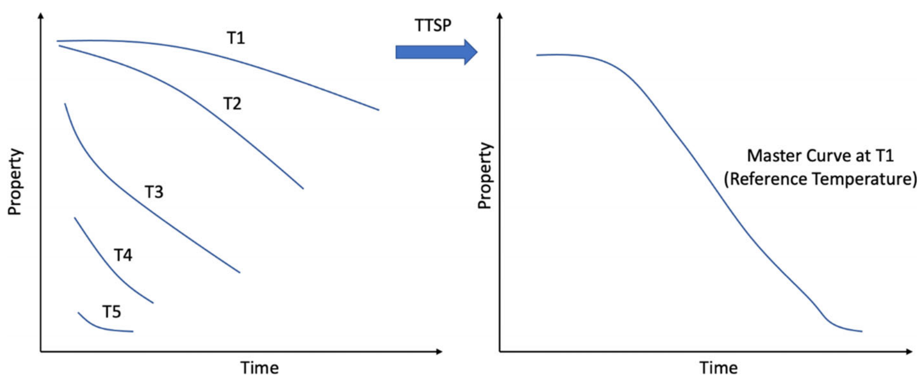


FIGURE 24 Schematic diagram for constructing a master curve by TTSP. Adapted with permission.[120] Copyright 2012, Elsevier. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 4 High-performance fibers' sensitivity to various aging factors.

| | Sensitivity to aging factors | | | | |
|---|---|---|---|---|---|
| Fiber | Heat | UV | Moisture | Abrasion | Laundering |
| Para-aramid | Moderate | High | Very high | Low | Very high |
| Meta-aramid | Low | Very high | Not at all | Moderate | Not at all |
| Technora® | No information | No information | Not at all | No information | No information |
| PBO | Low | Very high | High to moderate | Very low | Moderate |
| PBI | Low | Moderate | Low | Low | No information |
| LCP | Very high | Very high | Low | No information | No information |

is calculated by constructing a master curve produced by shifting all the experimental data onto the data at a reference temperature. An illustration of the process of constructing a master curve is given in Figure 24.

Researchers have found that the TTS principle applies to textiles, including fire-protective fabrics.[38,54,59] However, the use of the TTS principle rests on the following three conditions[119]: (i) the shapes of adjacent curves are identical in a semi-logarithmic plot, (ii) the shift factor for all viscoelastic functions is the same, (iii) a reasonable Arrhenius plot can be constructed from the temperature dependence of the shift factors. However, if a material is exposed around its glass transition temperature (Tg), the energetically- and entropically-induced relaxation may make the material deviate from the TTS principle. Furthermore, in the case of inhomogeneous polymers or materials involving a polymer blend, the TTS principle sometimes does not apply.

### 5.3 | The Hill equation

Researchers have also used the three parameter Hill equation in combination with the Arrhenius model for quantifying the kinetics of material's aging.[59,121] For instance, Dolez et al.[59] employed the Hill equation to determine how aging time affected the residual tearing strength of thermally aged fire-protective fabrics.

The Hill equation (Equation 3) has three parameters that can describe a nonlinear relationship between two variables.[122] In the polymer aging field, researchers have successfully used the Hill equation to fit sigmoidal curves.

$$y = \frac{y_{max} x^{\alpha}}{c^{\alpha} + x^{\alpha}} \tag{3}$$

In the equation, the three adjustable parameters are $y_{max}$, $c$ and $\propto$ whereas $x$ and $y$ refer to the independent and dependent variable, respectively. Apart from material's aging, the Hill equation is widely used in pharmacology and bioscience research area.[122,123]

## 6 | DISCUSSION

### 6.1 | Correlation between the nature of high-performance fibers and the impact of the aging factors

Different aging factors to which firefighters' protective equipment is constantly exposed, including heat, UV, moisture, abrasion and laundering, affect the performance of fire-protective fibers. Determining which aging factor(s) has the most significant impact on each fiber is critical to help designing the best performing blends. Table 4 provides a rating of the sensitivity of a series of high-performance fibers used in fire-protective fabrics to various aging factors.

For instance, para-aramid fibers appear more susceptible to moisture than to other aging factors. Particularly, para-aramid fibers experience substantial hydrolytic degradation in the presence of an acid catalyst, according to the findings of Hoque et al.[54] Thus, this fiber is sensitive to exposure to atmospheric moisture, water immersion, and laundering. Since the amide linkage in the fiber efficiently absorbs UV light, the para-aramid fiber is also sensitive to UV.[4,49,50] On the other hand, the para-aramid fiber is less susceptible to thermal aging because of its high decomposition temperature of 590°C.[11,59] In addition, para-aramid fibers do not appear to be very sensitive to severe abrasive cycles according to a table prepared by Bollschweiler et al.[124] based on previously published studies.

Contrary to para-aramid fibers, meta-aramid fibers have a low sensitivity to hydrolytic aging despite having a very similar chemical structure.[54,55] This may be due to the higher flexibility of the meta-aramid polymer chain which allows a tighter packing and restricts water penetration.[65] Consequently, this fiber resists well exposure to atmospheric moisture, water immersion, and laundering. However, the meta-aramid fiber is slightly more UV-sensitive than para-aramid. According to Houshyar et al.,[60] a variation in the skin-core structure between para-aramid and meta-aramid fibers is the cause of their different UV sensitivity. In comparison, the meta-aramid fiber has a thinner skin, allowing UV irradiation to quickly affect the fibers' core crystalline area, resulting in rapid UV degradation. Meta-aramid fibers, on the other hand, have been found to have a low vulnerability to thermal aging with a constant operating temperature of 200°C.[11,59] Finally, according to Bollschweiler et al.,[124] meta-aramid fibers are moderately vulnerable to repeated abrasion.

Similar to meta-aramid, Technora® fibers do not degrade much when exposed to moisture,[125] indicating that it is not susceptible to hydrolytic degradation. This may be due to Technora®'s manufacturing process, which does not rely on strong acid and only uses the super drawing technique during fiber formation,[126] thus leaving no sulfur residues, which have been reported to lead to acid aqueous media and acceleration of hydrolysis in aramid fibers.[54] It is not possible to comment on the sensitivity of the Technora® fiber to thermal, UV, abrasion and laundering aging due to the lack of data on the resistance of this material to these aging factors.

Heat does not affect PBO fiber much as the fiber possesses a high decomposition temperature (600°C).[11,59] On the other hand, this fiber has been reported to be sensitive to moisture. In fact, moisture-induced degradation of the PBO fiber was pointed at as the potential cause for the premature failure of a PBO fiber-based body armor.[24,127] However, recent accelerated hydrothermal aging studies on PBO fiber-based fabrics involving water immersion and laundering did not evidence any strong sensitivity of PBO fibers to moisture.[55,72] In the case of UV radiation, a higher sensitivity was reported for PBO compared to aramid fibers.[128] According to a compilation of results from the literature by Bollschweiler et al.,[124] the PBO fiber has a good resistance to repeated abrasion.

Compared to aramid and PBO fibers, PBI fibers are more resistant to UV aging (PBI Performance Products, n.d.).[129] In addition, they are not thought to be moisture sensitive due to the strong aromatic structure of the PBI molecule.[41] Moreover, with a high decomposition temperature at 580°C,[11,59] these fibers are supposed to resist well to thermal aging. PBI fibers, on the other hand, have a low mechanical strength,[130] which suggests that they will also have a low abrasion resistance. In addition, the high sulfur content in PBI fibers was linked to the large loss in strength of para-aramid/PBI fabrics upon hydrothermal aging[54]; the acidic conditions the PBI fibers create when exposed to water accelerate the hydrolysis of the para-aramid fibers with which they are often combined in firefighter protective clothing to compensate with their low strength.

The LCP fiber has been reported to be very vulnerable to UV aging conditions[77] while being fairly resistant to hydrothermal aging.[78] LCP fibers are susceptible to thermal aging.[131] In addition, LCP fibers melt above 350°C, which limits their use in protective equipment for firefighters to low fiber contents. To the best of the author's knowledge, there is no information available on the behavior of LCP fibers during repeated abrasion and laundering.

## 6.2 | Accelerated aging program and relevance to the real firefighting scenarios

When conducting accelerated aging studies, it is crucial to consider the acceleration factor and keep the aging program as close to the typical service conditions as possible. During research on the aging of firefighters' protective clothing, a variety of aging programs, including exposure to heat, UV, and/or moisture, have been used. For instance, researchers have employed short-term radiative and longer-term convective heat exposure techniques to examine the thermal aging behavior of high-performance fiber-based firefighters' protective clothing. However, experiments with radiative heat exposure involve highly accelerated thermal aging circumstances, with a duration of a few minutes at most, while the recommended lifespan of a firefighter's protective equipment is ten years based on NFPA 1851.[100] The very high acceleration aging factor resulting from this large discrepancy in the aging timeline between radiative heat accelerated aging programs and the actual service conditions may result in different aging processes/mechanisms taking place in the specimens subjected to accelerated aging compared to service use. As a result, we suggest to opt for month-long accelerated aging programs rather than much shorter ones when evaluating the aging of high-performance fibers used in firefighters' protective clothing.

In terms of UV aging conditions, accelerated aging research of high-performance fibers has been conducted using various weathering apparatuses equipped with carbon arc, xenon, and fluorescent lamps at different irradiance levels between 0.24 and 1.55 W/m$^2$ and temperatures between 40 and 80°C for up to 66 days (Section 4.2). As the purpose of UV aging should be to replicate the type of UV exposure that firefighters experience, the use of carbon arc lamps seems dubious given the considerable difference in spectra between carbon arc lamps and sunlight and the resulting high likelihood of unrealistic material degradation processes induced with carbon arc lamps.[132,133] Aging experiments using xenon and fluorescent lamps each have their unique advantages. For instance, xenon lamp weathering machines can produce the whole spectrum of sunlight, while fluorescent lamp weathering machines only apply UV at lower wavelengths (365 nm and downwards),[134,135] which is representative of the conditions experienced during bunker gear storage in lighted rooms. In addition, it is critical to use irradiance levels that are not too far away from the actual conditions experienced in service. According to the ASTM G173-03[136] standard, the average direct normal irradiance in the afternoon at 37°C for a sun-facing tilted surface is 0.2966 W/m$^2$ at a 340 nm wavelength. Keeping that in mind, the exposure of fabric specimens to 1.55 W/m$^2$ may be too far away from actual service conditions and lead to degradation processes/mechanisms that would not be relevant to the way high-performance fibers used in fire-protective protective clothing would degrade in real life.

To research how moisture affects firefighters' protective clothing, two types of accelerated aging protocols can be found in the literature (Section 4.3). One method is to expose the specimens to atmospheric moisture at elevated temperature; values of relative humidity between 37 and 76% and temperature between 50 and 90°C have been observed in published studies. The second method involves submerging the samples in heated water,

TABLE 5 Example of comprehensive accelerated aging (individual and combined) program relevant to firefighters' protective clothing.

| Aging condition | Temperature | RH /water | UV (irradiance at 340 nm) | Abrasion | Laundering | Experimental plan |
|---|---|---|---|---|---|---|
| Heat | 90, 150, 190, 220, 275, 300, 320°C | - | - | - | - | Exposure of up to 1200 h for the lowest temperatures and up to 500 h at the higher temperatures using an air circulating oven. |
| Liquid water | 40, 60, 80, 90°C | Water immersion | - | - | - | Specimens fully immersed in heated water kept in an air circulating oven for up to 1200 h |
| Atmospheric moisture | 60, 80, 90°C | RH- 50, 70, 100% | - | - | - | Exposure of up to 1200 h |
| UV | 40, 60, 80°C | - | 0.35, 0.68, 1, 1.35 $W/m^2$ | - | - | Exposure for up to 600 h |
| Abrasion | - | - | - | Taber abrasion | - | Repeated abrasion for up to 1000 cycles |
| Laundering | 40, 60°C | - | - | - | Domestic washing + air drying | Repeated laundering for up to 50 cycles |
| Heat + UV + RH applied simultaneously | 40, 60, 80°C | RH of 50, 70, 100% | 0.35, 0.68, 1, 1.35 $W/m^2$ | - | - | Exposure for up to 600 h |
| Heat + UV and Water spray applied alternatively | 40, 60, 80°C | Water spray | 0.35, 0.68, 1, 1.35 $W/m^2$ | - | - | Alternation of 4 h of heat + UV and 1 h of water spray for up to 600 h |
| Abrasion and Laundering applied alternatively | Laundering at 40 and 60°C | - | - | Taber abrasion | Domestic washing + air drying | Repeated cycles of 100 abrasion cycles and 6 washing cycles, for a total of 500 abrasion cycles and 30 laundering cycles |
| Heat, UV + RH and Abrasion applied alternatively | Heat only segment at 90, 150, 220°C | RH- 50, 70% | 0.35, 0.68 $W/m^2$ at 60°C | Taber abrasion up to 300 cycles | - | Alternating sequences of exposure to heat, UV + RH, and abrasion |
| Heat, UV, Water Spray and Abrasion applied alternatively | Heat only segment at 90, 150, 220°C | Water Spray | 0.35, 0.68 $W/m^2$ at 60°C | Taber abrasion up to 300 cycles | | Alternating sequences of exposure to heat, UV, water spray and abrasion |
| Heat, UV + RH, Abrasion, and Laundering applied alternatively | 90, 150, 220°C | RH- 50, 70% | 0.35, 0.68 $W/m^2$ at 60°C | Taber abrasion up to 300 cycles | Domestic washing + air drying up to 30 cycles | Alternating sequences of exposure heat, UV + RH, abrasion, and laundering |
| Heat, UV, Water Spray, Abrasion, and Laundering applied alternatively | 90, 150, 220°C | Water spray | 0.35, 0.68 $W/m^2$ at 60°C | Taber abrasion up to 300 cycles | Domestic washing + air drying up to 30 cycles | Alternating sequences of exposure to heat, UV, water spray, abrasion, and laundering |

typically between 60 and 90°C. Water immersion techniques generally results in more severe aging compared to air moisture-based hydrothermal aging.[70]

Another aspect to consider is the fact that firefighters work in situations where their protective clothing is exposed to several different aging factors, applied either simultaneously, for instance moisture and heat at a fire scene or during washing, or alternatively when the weather alternate between rain and sun.[104] These different aging factors may act in synergy to further reduce the performance of the fabrics. Yet, most studies only considered the effect of aging conditions applied individually and thus do not describe appropriately the reality of the fire-protective clothing aging in service.

Therefore, it is important that accelerated aging studies conducted on firefighters' protective clothing expose specimens to different aging factors simultaneously and alternatively depending on the case and use types, intensities and durations of exposure relevant to typical service conditions so that the data generated simulate more realistically the loss in performance experienced in service by firefighter protective clothing. An example of comprehensive aging program is proposed in Table 5. It includes individual and combined aging conditions, with aged specimens being collected at regular intervals to have their residual performance being assessed.

As shown in Table 5, different exposure conditions have been proposed for the aging program. The temperatures for the thermal aging range between 90 and 320°C. It considers the continuous operating temperature of 190–250°C for high-performance fibers typically used in firefighters' protective clothing[11,59] and the range of firefighter exposure conditions (60–300°C for routine conditions).[137,138] The ranges of UV irradiance have been chosen based on typical UV irradiance levels observed outdoors. For instance, irradiances of 0.55 W/m$^2$ are typically observed in Toronto, Canada at noon in July,[139] and the average irradiance of the sun is 0.2966 W/m$^2$ at 340 nm.[136]

Exposure to moisture is applied using liquid water (applied by immersion and through water spray) and atmospheric moisture. Exposure to liquid water by immersion and spray has been proposed considering firefighters' work with water as fire extinguishing medium and the effect of rain and snow. During laundering, protective gear is also immersed in water. It may also be soaked with the perspiration of the wearer. In addition, the working environment of firefighters may also involve different levels of relative humidity from the weather, for example, in the summer in Montreal, Canada, or steam generated from heated water and burning objects. The proposed accelerated aging program would also allow comparing the aging behavior of high-performance fibers used in fire-protective fabrics due to water immersion and atmospheric moisture.

In terms of abrasion, there is still very limited data available. The ultimate number of 1000 abrasion cycles proposed considers the recommended lifetime of ten years for firefighter protective clothing.[100] In terms of laundering, the current number of recommended advanced cleaning of two per year is expected to increase due to concerns about the accumulation of fire-generated carcinogenic compounds in the fabric layers of fire-protective suits and their negative effect on firefighters' health. Firefighter protective suits may end-up having to be washed after each fire-involving operation: the proposed number of 50 laundering cycles would correspond to one advanced cleaning a week for one year.

Finally, the comprehensive plan proposed in Table 5 includes several combinations of different aging factors in addition to conditions involving individual factors with the eventual use of heat as an accelerating factor. Depending on the case, these combined conditions are applied simultaneously such as for UV and atmospheric moisture or alternatively such as laundering and abrasion. The information provided by all these individual and combined aging tests will help identify which aging factor(s) control the combined aging conditions. It is expected that the response will vary depending on the fiber.

### 6.3 | Test plan for evaluating the residual performance of high-performance fabrics used in the Firefighters' protective clothing after accelerated aging

According to the specification NFPA 1971,[7] the composite (3-layers assembly or whole ensemble) of the firefighters' protective clothing shall fulfill requirements in terms of TPP, THL, and liquid penetration. In addition, the outer shell fabric shall pass the flame resistance, heat resistance and thermal shrinkage, tear resistance, tensile strength, cleaning shrinkage resistance, and water absorption resistance tests. Furthermore, the moisture barrier shall satisfy requirements in terms of tear resistance, cleaning shrinkage resistance, water resistance, liquid penetration resistance, and resistance to light degradation. The thermal liner shall pass the tear and shrinkage resistance test. The seam-breaking strength is also tested on all seam assemblies of the garment. The requirements of NFPA 1971[7] can thus serve as a basis for the assessment of the residual performance of firefighters' protective clothing fabrics after accelerated aging.

However, prior studies have shown that some of these performance do not appear to be significantly

**TABLE 6** Proposed list of tests for evaluating the effect of aging on firefighters' protective clothing performance.

| Test type | Test method | Rational |
|---|---|---|
| Mechanical performance | 1. Tensile strength, and/or<br>2. Tear strength.<br>NFPA 1971[7] recommends ASTM D5034 and ASTM D5587 for tensile and tear resistance tests, respectively. In the case of limitations in material availability, the ASTM D5035 test can be used instead of ASTM D5034 as the specimen size is smaller. Also, for the tear strength, it has been shown that a smaller specimen size can be used for ASTM D5587 without significantly affecting the test results.[140] | The mechanical properties of high-performance fibers-based firefighters' protective clothing are critically get affected due to aging.[37,58,93] |
| Barrier performance | 1. Water penetration resistance, and/or<br>2. Water absorption<br>3. Water contact angle.<br>4. Water resistance by hydrostatic pressure.<br>5. Liquid penetration resistance<br>6. Water vapor permeability<br>NFPA 1971[7] standard recommends the AATCC 42 test method for assessing the water resistance of outer shell fabrics. In the case of fabric scarcity, the ISO 9073-6 test for liquid absorbency and/or the water contact angle measurement can be performed instead.<br>For the moisture barrier, NFPA 1971 offers to conduct either test method FS 191A TM 5512 or ASTM F903. In the case of specimen scarcity, the inverted cup ASTM E96 water vapor permeability test can be an option as this test requires comparatively smaller specimen size. | Aging was shown to affect the barrier performance of high-performance fibers-based firefighters' protective clothing such as water and liquid absorption.([37,54]) |
| Morphological Analysis | 1. Scanning Electron Microscopy (SEM), or<br>2. Scanning Helium Ion Microscope (SHiM).<br>An SEM either equipped with a Lanthanum hexaboride or a field emission gun is suggested for the morphological analysis of the aged fibers. A tungsten filament SEM machine is not recommended as small features like the initiation of fiber breakage could be hard to identify with the comparatively low-resolution it provides. However, as high-performance fibers are non-conductive, a conductive coating (gold or carbon) is needed, which may hide small features in the sample as well.<br>A SHiM can be an interesting alternative to SEM as this equipment can directly image non-conductive samples, thus avoiding the risk of burying small features in the aged fibers under a conductive coating. | Aging affects the morphology of high-performance fibers[60] |
| Chemical Analysis | 1. ATR- FTIR<br>2. X-ray Diffraction (XRD)<br>High-performance fibers cannot be easily made into a powder, so preparing KBr pellet for the conventional FTIR technique is not an option. Instead, the ATR-FTIR technique can be used as it requires no special sample preparation.<br>According to literature, the crystallinity peaks found in high-performance fibers are in the range between 10 and 45° angle. It is thus important that the XRD analysis of high-performance fibers-based firefighters' protective clothing is conducted over that range. | Chemical changes in aged high-performance fibers due to aging have been documented in several studies.[41,59] |

affected by aging. For instance, as reported in Section 4, most researchers did not observe any effect of aging on the flame and heat resistance, and thermal shrinkage of the fire-protective fabrics. It can possibly be attributed to the inherent flame and heat resistance of the high-performance fibers used in the firefighters' protective clothing. On the other hand, studies performed on used firefighter bunker suits reported strong decreases in strength and barrier properties. Studies conducted on specimens subjected to accelerated aging also evidenced changes in the fiber morphology and chemical composition.

Based on these information, a test plan is suggested in Table 6 to evaluate the residual performance of fabrics used in firefighters' protective clothing after accelerated aging. The same test plan can also be used for assessing the residual condition of used bunker gear.

### 6.4 | Research gaps and future directions

A significant amount of research has been done so far on firefighters' protective clothing, which has allowed the development of high-performance fibers and improved garment designs. However, the topic of materials' aging has been largely neglected, despite its critical importance, and many questions remain to be answered.

First, all of the research work has focused on the effects of specific conditions on the firefighters' clothing assembly. However, the important question of the useful lifetime of the firefighters' protective clothing has remained unanswered. Researchers have concluded their studies with findings showing the reduction in performance due to exposure to accelerated aging conditions but without coming up with a useful lifetime for the firefighters' fabric or clothing. On the other hand, although researchers who conducted a series of studies involving the post-use analysis of firefighters' clothing[30–33] concluded on the validity of the recommended useful lifetime of ten years for firefighter turnout gear, the researchers did not have access to the information about the conditions experienced by these turnout gear during their life. Yet, the conditions of use may largely differ based on the level of activity of the fire station and the position of the firefighter in their fire brigade. It is thus critical to develop predictive aging models of the useful lifetime of firefighters' protective clothing based on the conditions of use.

Second, innovation in terms of new fibers and improved fiber blends is limited by the fact that any failure can have dramatic consequences on firefighters' safety. At the same time, information about their long-term performance is generally only available when the bunker suits are retired after ten years. The identification of accelerated aging protocols combining the effect of the different aging conditions involved and simulating satisfactorily the loss in performance experienced in service by firefighters' protective clothing fabrics would be needed to provide a mean to generate data on new fibers and improved fiber blends in a timely manner and foster innovation in firefighter protective gear.

Finally, as the cleaning frequency of bunker gear is being gradually increased to try removing fire-related toxic chemicals from the fabric layers and preventing them from reaching the firefighter's skin or being resuspended in the air and inhaled. Therefore, the historical data on which the retirement age of firefighter bunker suits is currently based are unfortunately becoming obsolete due to the sensitivity of some fire-resistant fabrics to laundering. As a result, there is a critical need for tools to continuously monitor the residual performance of the fabrics without the need for destructive testing. One such strategy proposed is an end-of-life sensor based on combining a graphene-based conductive track with a sacrificial polymer sensitive to the same aging conditions as the fire-protective fabrics.[141,142] Upon aging, the sacrificial polymer develops cracks which disrupt the integrity of the conductive track and affect its electrical conductivity. The measurement of the resistance of the end-of-life sensor positioned on fabric patches at a few strategic locations on the bunker suit is conducted using a standard multimeter as part of the regular assessment that workers at risk of heat and flame exposure do of their protective equipment. The development of this end-of-life sensor for fire-protective fabrics is now getting into the scale up stage.[143]

## 7 | CONCLUSION

The different blends of high-performance fibers such as para-aramid, meta-aramid, PBI, and PBO are the basic raw materials for manufacturing many professionals' protective gear, including firefighters. Due to the nature of the job, firefighters frequently encounter various hazardous conditions from very close proximity. Firefighters' protective clothing is their last line of defense to keep them safe while protecting others. Since the firefighters' protective clothing, as any material, ages with time, it is crucial to understand and predict the effect of aging on the performance of the protective clothing of firefighters.

For the first time to the best of the authors' knowledge, this article reviews the main findings in terms of aging of high-performance fibers and fabrics used in firefighter protective clothing and discusses a path forward. Results obtained on used firefighter protective clothing, some of them still in used, showed large losses in tear strength for some outer shell fabrics after only two to three years of use. Some outer shells and moisture barriers used for less that the 10-year retirement time recommended by NFPA 1851 also failed to meet the minimum requirement of NFPA 1971 for water absorption resistance.

In terms of accelerated aging results, para-aramid fiber has been found to be sensitive to thermal, UV, and hydrothermal aging. If meta-aramid fiber was also affected by thermal and UV aging, it resisted well hydrothermal aging. Technora® fiber, which is an aramid copolymer, exhibited a strong resistance to hydrolytic aging. No information was found on its thermal and UV aging behavior. Regarding PBO fiber, conflicting results exist regarding its sensitivity to moisture. Finally, residual sulfur in PBI fibers leading to the accelerated hydrolysis of para-aramid fibers has been identified as the culprit for the large performance drop observed in para-aramid/PBI fabrics when exposed to moisture.

Researchers have mostly focused on the effect of aging on strength, which is often severely affected by aging. In a few instances, a degradation of the water repellent finish as a result of aging was reported. On the other hand, no impact on flame resistance was generally measured. Very few works have been found on the long-term effect of abrasion and laundry on the performance of these fabrics.

However, many questions remain about the aging of firefighters' protective clothing and different areas have been identified for further investigation: (1) in-depth study of the aging of some promising high-performance fibers such as Technora®; (2) analysis of combined aging conditions (either simultaneously or alternatively) to better replicate realistic use scenarios; (3) identification of accelerated aging programs simulating the result of service aging; (4) predictive aging models of the residual performance of fire-protective fabrics; and (5) monitoring tools (e.g., end of life sensors) of the fabrics's condition during service. More research is needed in this critical yet neglected area of high-performance fiber aging to ensure firefighters' safety.

## AUTHOR CONTRIBUTIONS

**Md. Saiful Hoque:** Conceptualization (lead); data curation (lead); formal analysis (lead); methodology (lead); visualization (lead); writing – original draft (lead). **Patricia Dolez:** Conceptualization (supporting); funding acquisition (lead); supervision (lead); writing – review and editing (lead).

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## DATA AVAILABILITY STATEMENT

As this is a review paper, data is available in the articles and other sources of information cited.

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