Deterioration of polyaramid and polybenzimidazole woven fabrics after ultraviolet irradiation

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ABSTRACT: In this study the degradation of woven fabrics of meta-aramid and the blend of para-aramid and polybenzimidazole fibers when exposed to environmental conditions has been investigated under accelerated ageing conditions. Generally, these polymeric materials have been used for the outer layer of protective clothing, particularly for fire-fighting. The performance of these fabrics plays an important role in preventing burn-injuries to fire fighters. Frequent exposure of these materials to various environmental conditions (especially sunlight) can degrade the polymeric chain and affect their performance properties. Hence, the degradation of the fabrics has been studied in terms of loss of tensile and tear strength; reduction in abrasion resistance; and extension at break. It was observed that ultraviolet (UV) irradiation negatively impacted on the mechanical properties of both the polymeric materials significantly. This can be attributed to chemical changes in the polymeric chains due to the photo-oxidation of the polymer. Scanning electron microscopy images revealed surface decomposition of the filaments due to UV irradiation. Exposure of polybenzimidazole resulted in rapid loss of mechanical and chemical properties in comparison with meta-aramid. However, decomposition and degradation of polybenzidimazole was not statistically significant. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43073.

INTRODUCTION

Fire-fighters encounter a range of physical and chemical hazards, and protective clothing is designed to safeguard them from these hazards.[1,2] A standard protective clothing system is designed as a multilayer construction consisting of outer layer, moisture barrier, and thermal liner. The outer layer is a shield against excessive heat and physical hazards common to fire fighting.[1,3,4] Depending on the type of activity and position of a fire-fighter in relation to the fire, this outer layer is exposed to a variety of environmental conditions.[1,5] There are several publications describing the impact of simulated environmental conditions, for example, thermal and ultraviolet (UV) exposure; and the level of usage, on the performance of fabrics similar to those used in fire-fighter protective clothing.[3,5–7]
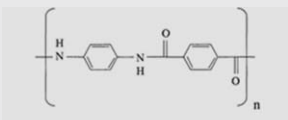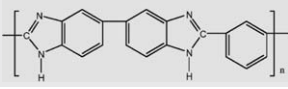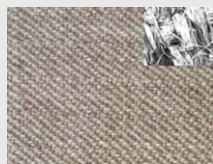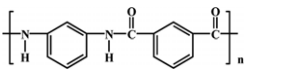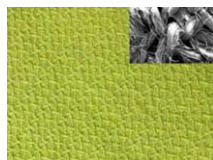
The outer layer of the protective clothing is usually exposed to environmental conditions such as UV, humidity and radiant heat from the Sun and fire.[1,4] Generally, these environmental conditions degrade the mechanical properties of the outer layer used in the protective clothing. Degradation of the mechanical properties could result in insufficient protection against hazards, which can lead to serious injuries to fire-fighters.[3,8–10] There-

fore, it is important to understand the effect of environmental conditions, especially UV radiation, on the performance and mechanical properties of the outer layer of protective clothing.[5,10,11]

Fabrics prepared from high tenacity fibers such as polybenzimidazole (PBI) and aramid are generally sensitive to light exposure. They suffer from significant loss of strength on exposure to UV radiation, due to bond scissions via free radical generation similar to many other commercially available polymers. The fabrics prepared from PBI fibers possess exceptional thermal stability, resistance to ignition and hydrolysis; however, they are susceptible to UV.[10–14]

Several studies had shown that polyaramids (p-aramids) such as Kevlar [poly(p-phenylene terephthalamide)], Nomex [poly(m-phenylene isophthalamide)], or PBI are sensitive to the UV radiation when accompanied by moisture and heat.[5,10,12] Dobb and Robson[15] reported that Kevlar 149 lost its protective and mechanical properties when exposed to UV irradiation. Toy and Stringham[16] confirmed similar results with Kevlar 29. Recently, Davis *et al.*[17] reported a dramatic loss in mechanical and chemical properties of outer layer fabrics used for fire-fighter protective clothing after exposure to UV irradiation in the presence of

Table I. Detailed Properties of Fabric A and B. [Color table can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Fabric	Areal density (GSM)	Thickness (mm)	Chemical structure	Weave	Picture
A	218	0.47		Rip-stop	
B	224	0.75			

moisture (50% relative humidity) and heat (50°C). It was observed that the tear strength and tensile strength of the poly-aramid and polyaramid/polybenzimidazole based fabrics decreased by more than 40% after 13 days of exposure to these conditions. The fabric containing PBI was less influenced by these conditions as it maintained approximately 20% more of its mechanical properties. Arrieta et al.[18] investigated the photo-degradation of PBI by UV irradiation process, which was characterized by the shifting of the absorptions peaks in the UV spectrum toward higher wavelength.

There have been several publications investigating the impact of environmental conditions on high performance fibers used in fire-fighter's protective clothing or other protective gear.[4,10–12,15–19] For instance Carvalho et al.[4] investigated the controlled degradation of polypropylene containing pro-oxidant agents, and established that the addition of these agents promoted the oxidative thermal degradation of polypropylene. Zhang et al.[6] showed the linear deterioration of the mechanical properties of poly(p-phenylene terephthalamide) fibers by continuous UV irradiation over 145 h at $40 \pm 3°C$ and 45% RH. The effect of UV on the degradation and stability of high performance PBI membranes was investigated by Kushwaha et al.[10,11] It was established that the PBI polymers degraded by an oxidative mechanism of degradation. Tincher et al.[20] investigated the effect of UV exposure on mechanical properties of poly(m-phenylene isophthalate) fibers. The results exhibited that the fibers lost 90% of the tenacity after this exposure.

Standards such as AS/NZ 4967:2009[21] and AS/NZ 4399:1999[22] focus on the selection, care, and evaluation of fire-fighter protective clothing, recommend the disposal of the protective clothing based on simple visual inspection. However, it is difficult to estimate the useful lifetime of fire-fighter protective clothing by visual inspection, as most of the degradation is not visually detectable. For example, loss in tensile and tear strength due to prolonged usage, care and maintenance, and UV exposure is not detectable based on visual inspection and objective tests are required to confirm this loss.[5–9] Hence, an appropriate quantitative method is required to evaluate the end of life of these protective clothing.

The objective of this study was to perform accelerated UV aging experiments to investigate degradation of the outer layer of fire-fighter protective clothing due to UV radiation and moisture. The commercial outer layer fabrics, made from m-aramid and blend of p-aramid/PBI were irradiated with UV (wavelength 300 cm^{-1} to 400 cm^{-1}) at conditions similar to those expected for fire-fighter protective clothing in service (50°C and ∼50% RH), for sufficient amount of time (1, 3, 5, and 7 days).[5–9,23] The loss in mechanical properties of these outer layer fabrics such as tensile strength, elongation at break, tear strength, and abrasion resistance of the UV irradiated samples were evaluated and compared with the properties of the unexposed fabric samples. Scanning electron microscopy (SEM) was performed to evaluate the surface decomposition of the filaments due to UV irradiation. Fourier Transform Infrared (FTIR) spectroscopy was performed to identify types of chemical bonds and functional groups present in the structure of both the exposed and unexposed fabric samples as a function of exposure time. Thermogravimetric analysis (TGA) was performed to evaluate the thermal degradation as a function of environmental exposure. This comparison will determine the extent to which the outer layers could be damaged by these conditions, and the results can be used to estimate the in service life-time of the protective clothing.

EXPERIMENTAL

Materials

Two commercially available outer layer fabrics generally used for fire-fighter protective clothing, were used in this research. The nomenclature "A" and "B" were used for the fabrics made of 60% Kevlar/40% PBI and 100% Nomex, respectively. Both fabrics have a rip-stop woven structure of about 220 g/cm². Table I shows the construction parameters for fabric A and B.

Fabrics were stored in black plastic bags to avoid any possible UV degradation. The fabrics were conditioned and tested in a standard atmosphere with $65\% \pm 2\%$ RH and $20°C \pm 2°C$ temperature, unless specified. The plastic bags were not completely sealed during conditioning and they were conditioned at least

Table II. Tensile and Tear Strength of Fabric A and B Exposed to Intense UV Irradiation, Temperature, and Humidity

	Ageing time (days)	Max load at break (N)	Extension at break (mm)	Tear strength (N)
	0	1416 ± 120	19 ± 2	135 ± 3
	1	1301 ± 80	18 ± 3	82 ± 8
Fabric A	3	1085 ± 87	9 ± 1	56 ± 15
	5	934 ± 181	9 ± 2	46 ± 15
	7	937 ± 98	9 ± 1	44 ± 13
	0	1355 ± 170	39 ± 3	183 ± 9
	1	1061 ± 83	37 ± 2	157 ± 7
Fabric B	3	716 ± 115	24 ± 0	112 ± 10
	5	709 ± 63	23 ± 4	106 ± 7
	7	762 ± 135	23 ± 0	29 ± 4

for 24 h in the standard atmosphere. The mass per unit area (g/m^2) of the fabric was calculated as the mean of five readings of 10 × 10 cm specimens following ISO 3801-1977 standard test method. Fabric thickness was measured in a SDL digital thickness gauge (Model: IDU 25E) following ISO 5084:1996 standard. An average of 10 specimens was taken for each fabric.

The specimens were tested for mechanical, surface and chemical properties, to measure the changes with UV irradiation on the properties of the fabric. Both unexposed (control) and exposed (UV irradiated fabric) specimens were tested for tensile strength, tear resistance, abrasion resistance, and FTIR spectroscopy.

UV Irradiation
Rectangular specimens (20 cm × 5 cm) were prepared for each of the fabrics (in weft direction), and exposed to high UV irradiance in a weather-O-meter (ci 4000). Accelerated exposure of the fabric to high UV irradiance was carried out using a Xenon lamp system to produce a uniform UV flux in the environmental chamber at 340 nm. Specimens were exposed to UV radiation at 40°C and 50% RH for 10,080 min (ASTM G155[24]). Specimens were continuously exposed to UV irradiance dosage of 0.24 ± 0.01 W/m² and removed from the chamber after 1, 3, 5, and 7 days and tests were performed.

Mechanical Properties
Exposed and unexposed specimens were tested for tear strength according to ISO 4674-1(Method B: trouser tear test)[25] and tensile strength in accordance with ISO 13934-1 (Textiles—Tensile properties of fabrics—Part 1: Maximum force and elongation at maximum force using the strip method),[26] using a Universal Test Instrument (Instron Model 3300 Single Column). Five test specimens were used to measure tensile strength and tear strength in each fabric in weft direction. The mean of data for tear strength, tensile strength, and elongation at break was calculated using Bluehill software and reported.

Abrasion resistance was determined based on AS 2001.2.25.2-2006[27] using a Martindale Abrasion Tester (Determination of

abrasion resistance of fabrics by Martindale method—determination of specimen breakdown). The test was performed to assess the degree of physical degradation by abrasion, and the point of breakdown was determined. The specimens were mounted in a specimen holder with a foam backing, and each specimen was rubbed against a standard abradant with a semi-random Lissajous motion. A total weight of 0.595 kg was used during the test, which is equivalent to a nominal pressure of 12 kPa. Four circular specimens, cut to 38 mm diameter were tested for each fabric. Care was taken during the mounting of the specimens so that they lay flat against the mounting block. The final point of breakdown was determined visually when at least two threads were broken.

FTIR Spectroscopy
FTIR spectroscopy was performed to identify types of chemical bonds and functional groups in the structure of both the exposed and unexposed specimen as a function of exposure time. The FTIR spectra were collected using a PerkinElmer Spectrum-400 spectrometer. The number of scans per spectrum was 4 and the FTIR spectra were collected in the wavenumber range of 4000 cm^{-1} to 650 cm^{-1}.

Scanning Electron Microscopy (SEM)
The surface morphology of the fabrics was analyzed by field emission scanning electron microscopy (Quanta FE-SEM) with an accelerating voltage of 15 kV. The specimens were placed on stubs and coated with gold using a sputter coater (SPI Module). The current in the sputter coater was set at 18 DC mA for 60 s, giving an approximate coating thickness of 10 nm.

Thermogravimetric Analysis
Thermal degradation as a function of environmental exposure was characterized using TGA. Samples of approximately 5 mg were cut from each fabric and accurately weighed. A Perki-nElmer Pyris 1 TGA was used for the experiments. Temperature was scanned from 25°C to 850°C at 10°C/min under a nitrogen purge of 10 mL/min, with a switch to air with the same flow rate at 700°C. The mass loss after switching to air was due to combustion of carbon residue formed during the scan because of the high aromatic hydrocarbon content of the fibers. The TGA was calibrated using Curie temperature standards and a reference mass. The data were represented as mass fraction and its derivative with time, as a function of temperature.

RESULTS AND DISCUSSION

The deterioration of mechanical properties such as maximum load at break, extension at break and tear strength of the tested fabrics are shown in Table II. Figure 1 indicates the percentage loss of tear strength, stress at break, and strain at break for both fabric "A" and "B" after exposure to UV irradiation. It is evident from Table II and Figure 1 that the exposure to UV irradiation has negative effect on the mechanical properties of both the fabrics, which is statistically significant. From Table II it can be observed that as the exposure time increased, there was a gradual reduction in tensile strength (maximum load at break), extension at break and tear strength of exposed fabric. For example, fabric A and B lost 67% and 84% of their tear strength, respectively, after 7 days exposure to the UV irradiation.
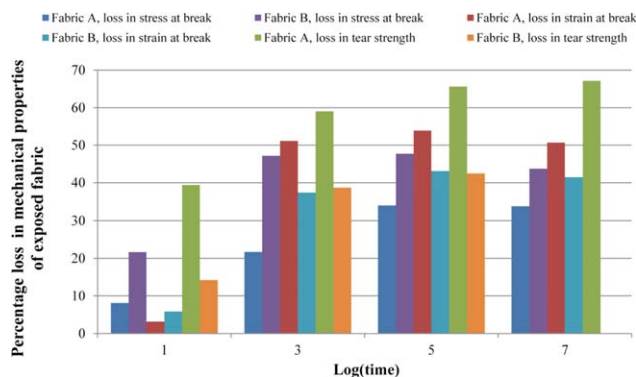
Figure 1. Loss in tear strength, stress at break, and strain at break for fabric A and B after UV irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Fabric B showed a rapid reduction of tear strength by 36% for the first 3 days of exposure, followed by much a slower deterioration rate for the subsequent 2 days. However, the deterioration of tear strength for fabric B was more severe when it exposed for 5–7 days, 65%, in comparison with fabric A, 42%. Better performance of fabric A in comparison with fabric B is attributed to the skin-core structure of the p-aramid (Kevlar) fiber,

with high core crystallinity and less ordered skin as UV irradiation easily affected the skin layer. Fabric B has little skin area and there is little difference between the structure of the skin and the inner (core) portion of the fiber. Therefore, Nomex$^{\circledR}$ (m-aramid fiber) is less stable than the Kevlar (p-aramid fibers).

Figure 1 indicates the deterioration of tensile stress and extension at break of the exposed fabrics. It is clear from the figure that both fabric A and B deteriorated in tensile stress and strain when the exposure time was increased. Fabric B showed higher reduction in tensile strength after seven day UV exposure, 45%, in comparison with fabric A, 34%. It is obvious from this figure that the strain at break decreased rapidly after seven days exposure to UV irradiation for fabrics A (51%) and B (42%), respectively.

The SEM images of the broken profile of both the exposed and unexposed specimens are shown in Figure 2. It can be observed from Figure 2 that the broken filaments in the yarn have a different profile than the control. This is attributed to the fact that after irradiation the ductile end of the filament became brittle. Zhang et al.[6] reported that the changes in the breaking mode indicate the etching effect of UV irradiation on the filament surface. Figure 2(a) confirms this finding for Kevlar/PBI blend (fabric A), as the end of the broken filament changed from fibril splitting to brittle. Figure 2(b) demonstrates the same
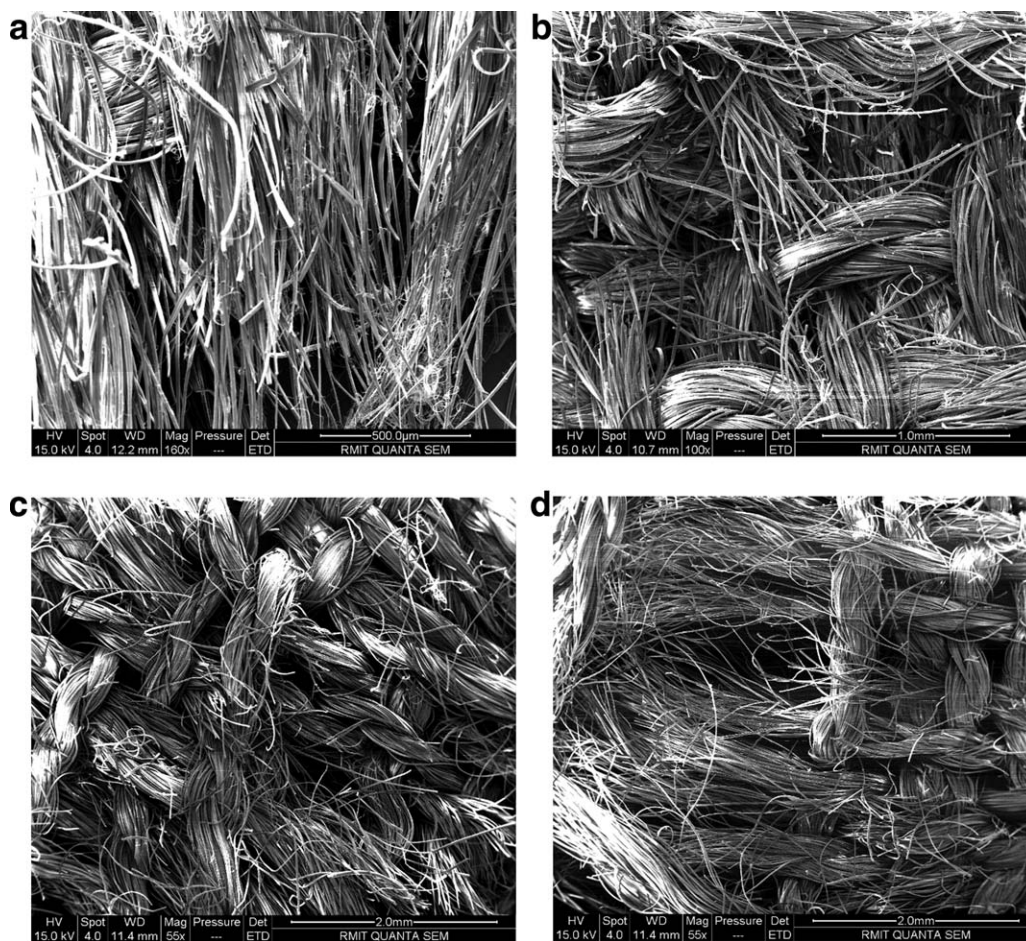

Figure 2. SEM images of the exposed and unexposed broken filaments after tensile or tear tests: (a) unexposed fabric A, (b) exposed fabric A, (c) unexposed fabric B, and (d) exposed fabric B.
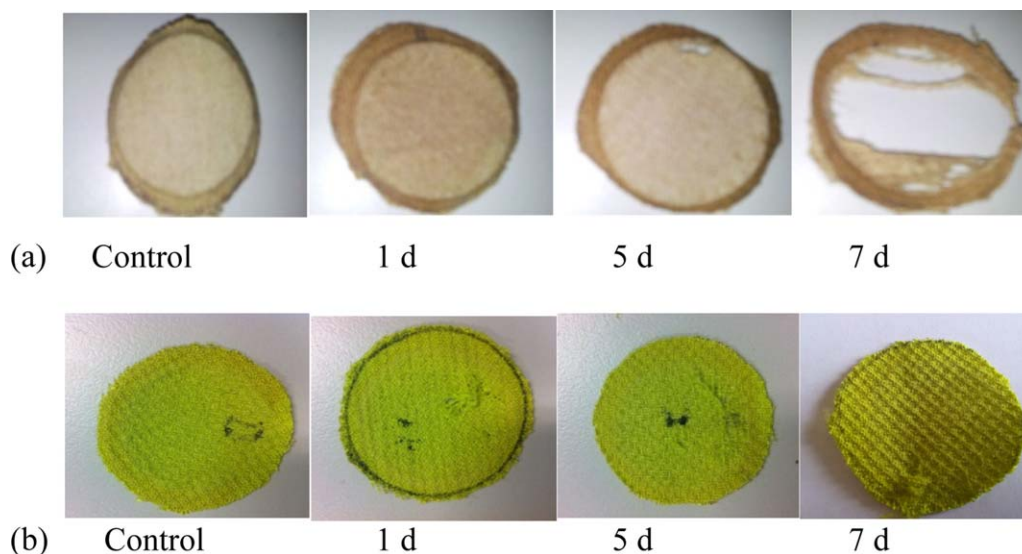
Figure 3. Abrasion test results for (a) fabric A and (b) fabric B exposed to UV irradiation for 1, 5, and 7 days. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

phenomenon for *m*-aramid (nomex) filament (fabric B), except the fracture end morphology is dependent on the exposure time, and the surface etching and roughness is more visible for the filament exposed for the longer time. In the case of *m*-aramid (fabric B) the UV irradiation started degrading the skin of the fiber and then initiated degradation to the inner part of the fiber. This led to obvious changes in the tensile failure mode, and quick loss of energy at break and elasticity.

Nazare *et al.*[5] reported similar mechanism for PBI exposed to UV irradiation. Degradation started at the skin, and the initiated crack in the skin propagated into the defected area of the core resulting in brittle failure mode. SEM images of the broken filament in Figure 2 is an evidence for these phenomena, which results in a rapid loss of tensile strength and extension at break.

Abrasion resistance of fabric was measured after 15,000 cycles at a pressure of 12 kPa. Figure 3 shows the fabrics after abrasion tests for each time. It is clear that exposure to UV radiation even for 1 day reduced the abrasion resistance of the fabrics, with multiple threads broken, especially the *m*-aramid filaments. Although the unexposed fabrics showed a slight color change, no broken thread was observed after 15,000 cycles. After seven days of UV exposure, fabrics A and B were disintegrated, as shown by the multiple broken threads, which indicate a substantial decrease in the abrasion resistance of the fabrics.

FTIR spectra of fabric A and B are shown in Figure 4. Main FTIR spectra peaks for original Nomex and Kevlar/PBI are as follow: 3310 cm^{-1}, 3060 cm^{-1}, and 1640 cm^{-1} associated to N—H stretching of amide, C—H stretching of aromatic rings and stretching of aromatic ring (C=C), respectively. The key FTIR peaks for PBI are special peaks at 3050 cm^{-1} and 1620 cm^{-1} that are related to aromatic N—H and C=C/C=N stretching and the benzene ring vibration at 1050 cm^{-1}.[28–32] The changes in the peak location and concentration indicate photo-oxidation of the polymer due to the possibility of formation of alcohol, acid, and amine.

It is observed in Figure 4 that exposure to UV radiation of fabrics A and B resulted new peaks indicating formation of alcohol, acid, and amine. Broadening with higher intensity of the peak at 3310 cm^{-1} ranging from 3000 cm^{-1} to 3500 cm^{-1} indicates formation of O—H and overlapping with N—H stretching. This was due to degradation of the amide backbone linkage after exposure to UV (photo-oxidation) and increased for the polymer with longer exposure time. This observation was confirmed by the conversion of amide peak to carboxylic acid/ester at 1610 cm^{-1} (C=O stretching).

The growth of broad stretching peak in the carbonyl region is an evidence of oxidative photo-degradation of polymer B. Other evidences were presence of the signal at 1640 cm^{-1}, 1710 cm^{-1}, and 1750 cm^{-1} which might correspond to the C=O stretching vibration of ketones and carboxylic acid, which were possibly formed as a result of photo-irradiation. Consequently, the possible formation of this carbonyl functional group helps in chain scissions and lowering down the molecular weight of the polymer.[10,17] As it can be seen from this figure, there is a shoulder peak at 1750 and 1770 cm^{-1}, which might be assigned to the formation of a small amount of aldehyde terminated chains and possible formation of aryl carbonates.[10,17,30] Figure 4(b,d) showed the difference between the chemical structures of polymer A and B after UV exposure for various ageing time. This figure confirmed the explanation from Figure 4(a,c) regarding the chemical chain cleavages due to the UV exposure.[17] However, further investigation is required to understand the details of chemical changes after UV exposure and the mechanism for this phenomena.

Nomex (*m*-aramid) degraded more rapidly for the first few days and then degradation slowed for the remaining exposure,[5,6,28,29] while PBI degraded slowly at the beginning but rapid up by time. The degradation of polymer A and B confirmed by Figure 4(b,c), which showed the structural changes of the polymer by exposing to UV. Further to this explanation, TGA results in the next section confirmed these polymer structural changes.

Figure 5 shows the results for TGA analysis of the two fabrics, A and B. From this graph both fabrics were found to lose

weight significantly after 360°C, due to thermal degradation. A weight loss of 4%–5% was seen in both fabrics exposed and unexposed before 100°C suggesting a volatile component, possi-
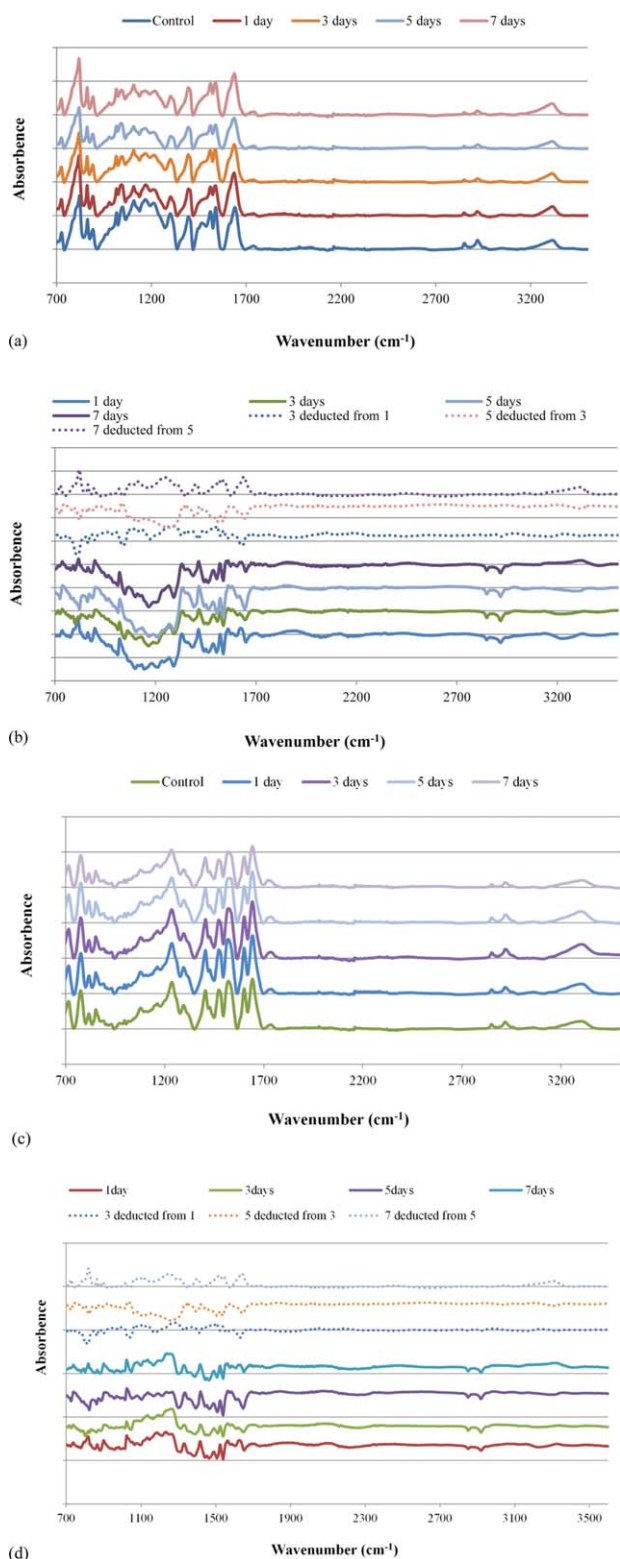

Figure 4. FTIR spectra of fabric A (a,b) and fabric B (c,d) as a function of ageing time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
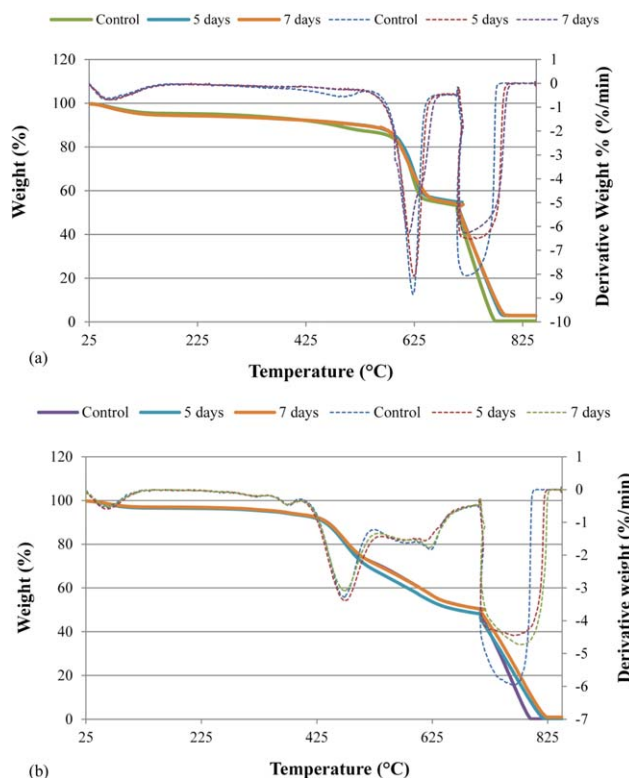

Figure 5. TGA results of (a) fabric A and (b) fabric B. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bly water, being removed from the materials. There were two distinct degradation steps, one with offset of 360°C and the other with offset at 550°C. Exposed PBI for 5 and 7 days showed a lower degradation rate at the first and second steps in comparison with the original fabrics.

Fabric A showed thermal stability until 550°C as it lost weight of less than 10%. However, by passing 550°C–700°C, there was a huge reduction about 34%. This means first molecular chain scission occurred and then radicals were produced in the process of degradation resulting in cleavage of benzene rings. Therefore, the derivative peak, 620°C, which resulted from benzene ring degradation, is smaller for exposed polymer due to the early degradation of UV exposed fabric. By switching from nitrogen to air, carbonaceous residue due to the thermal degradation of aromatic parts oxidized resulting in mass loss at 700°C of nearly 50%. The same condition occurred for Nomex (fabric B), to 390°C, there is not a huge weight loss and Nomex is more stable than PBI, however by passing that temperature (between 390°C and 520°C(, there was a sharp reduction in mass, 22%. By switching from nitrogen to air, carbonaceous residue from Nomex backbone and aromatic group degradation oxidized at this temperature and results in mass loss of nearly 51%.

CONCLUSION

The performance level of *m*-aramid, and blend of *p*-aramid and polybenzidazole fabrics, used in fire-fighter protective gear, has been investigated, after exposure to UV irradiation for various times. The mechanical performance, physical, and other chemical properties are affected by environmental conditions. It is

important to know the degree of loss in the performance level of these polymeric materials when exposed to sunlight (UV radiation) as the outer layer of protective clothing generally made of high performance polyamides/polybenzidazole. It was observed that the polymers exposed to high UV irradiation even for one day suffered loss in the tear strength, tensile strength, extension at break, and abrasion resistance. After exposure to 7 days, accelerated UV exposure, significant loss in mechanical properties of the fabrics was observed. Fabrics with m-aramid and p-aramid/PBI had 65% and 84% reduction in tear strength, respectively. Tensile strength and extension at break followed the same trend, with reduction of more than 40%. Abrasion resistance also gradually dropped after 1, 3, 5, and 7 days of exposure to UV. However, this reduction was greater for m-aramid in comparison with p-aramid/PBI blend.

FTIR spectroscopy and TGA results had been used to measure and interpret the chemical changes in the fabrics after exposure. FTIR results showed the possibility of aramid cleavage due to UV exposure, which could lead to production of reactant groups in the presence of moisture and heat and in consequence, chain cleavage. The results were supported by TGA data that explained the reason for deterioration of mechanical properties of filaments when exposed to UV irradiation. SEM images demonstrated the surface decomposition, deterioration, and roughness after exposure leading to a brittle failure mode. The loss in the mechanical properties can negatively impact on the protection performance from flame and physical threats. Therefore, it is important to store the protective clothing, when not in use away from the direct sunlight. Furthermore, tests should be performed at specific time intervals to check the loss of mechanical properties and hence the performance.

ACKNOWLEDGMENTS

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