

Effect of Artificial Perspiration and Cleaning Chemicals on the Mechanical and Chemical Properties of Ballistic Materials*

Joannie Chin,¹ Sylvain Petit,¹ Amanda Forster,² Michael Riley,² Kirk Rice²

¹Polymeric Materials Group, Materials and Construction Research Division, Building and Fire Research Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

²Office of Law Enforcement Standards, Electronics and Electrical Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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ABSTRACT: During routine field use of soft body armor, the ballistic panels become saturated with perspiration. This condition motivates the user to clean and/or deodorize the armor, and anecdotal evidence is given for various methods used to accomplish this. Although the cleaning/deodorization is usually performed on the armor liners and coverings, there is concern that the chemicals could seep into the ballistic panels and damage the fibers. The purpose of this study was to assess the effect of artificial perspiration and cleaning chemicals on the mechanical and chemical properties of aramid, poly(*p*-phenylene benzobisoxazole), and ultrahigh-molecular-weight polyethyl-

ene yarns after controlled cycles of exposure to artificial perspiration and dilute solutions of common cleaning chemicals. It was observed that the effect of the artificial perspiration on the properties of all of the materials tested was the same as that of water alone. Of all of the cleaning chemicals used, only chlorine bleach had a detrimental effect on the yarn properties. All other cleaning chemicals had the same effect as water alone. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 567–584, 2009

Key words: degradation; fibers; infrared spectroscopy; microstructure; strength

INTRODUCTION

Standard soft body armor is composed of multiple layers of ballistic fabric sealed into a woven fabric liner (referred to as the covering); this entire assembly is then inserted into a fabric carrier.^{1,2} During routine field use of soft body armor, the ballistic panels become saturated with perspiration. Although human perspiration is primarily composed of water, it also contains small quantities of organic compounds and inorganic salts. In the testing and qualification of body armor, questions have arisen as to whether human perspiration has an equivalent effect on the long-term properties of ballistic materials as plain water.

In attempts to clean and deodorize body armor, anecdotal evidence exists that vest users have sprayed the panels with odor neutralizer, disinfecting sprays, and cologne and/or wiped them down with dilute solutions of detergent or bleach. The laundering of ballistic panels and coverings is not recommended by body armor manufacturers or by the National Institute of Justice, who publishes standards for the testing of body armor.³ The carriers, however, can be washed and dried with conventional home laundering techniques.

The purpose of this study was to assess the effect of artificial perspiration and dilute cleaning chemical solutions on the mechanical and chemical properties of aramid, poly(*p*-phenylene benzobisoxazole), and ultrahigh-molecular-weight polyethylene ballistic yarns and fabrics with controlled cycles of exposure.

Correspondence to: J. Chin (joannie.chin@nist.gov).

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Certain commercial equipment, instruments, and materials are identified in this article to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by NIST, nor is it intended to imply that the materials or equipment identified are necessarily the best available for this purpose.

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OVERVIEW OF THE MATERIALS

In this study, three main classes of commercial ballistic polymers used in body armor were studied: poly(*p*-phenylenebenzobisoxazole) (PBO), poly(*p*-phenylene terephthalamide), and ultra-high molecular weight of polyethylene (UHMWPE). The tensile properties of these materials, as provided by their manufacturers, are shown in Table I.

TABLE I
Summary of Ballistic Fiber Tensile Properties
(Supplied by the Manufacturer)

	Density (g/cm ³)	Tensile strength (GPa)	Elongation at break (GPa)	Modulus (GPa)
Aramid yarn	1.44	2.8	3.7	70
PBO yarn	1.54	5.8	3.5	180
UHMWPE yarn	0.97	3.6	—	115–120

PBO is a member of the benzazole polymer family and is characterized by the heterocyclic benzobisoxazole group in its main chain structure, as shown in Figure 1. The conjugated benzobisoxazole and phenyl rings in the PBO repeat unit contribute to extended π -electron delocalization and molecular rigidity, which provides high thermal stability and outstanding mechanical properties to this class of rigid rod polymers. The PBO manufacturing process⁴ involves dry-jet wet spinning from a poly (phosphoric acid) solution. PBO fibers, like the majority of polybenzazole-based fibers, are extremely strong, tough, and stiff, with tensile strengths and moduli superior to those of aramid or UHMWPE. As is the case with rigid rod polymers, the compressive strength of PBO is relatively poor, being approximately 10–15% of its tensile strength.⁵

Previous research on the chemical resistance of PBO has documented significant losses in tensile strength after immersion in 100°C water, 121°C sodium chloride solution, and room temperature hydrochloric acid, nitric acid, sulfuric acid, and sodium hypochlorite.⁶ In a study of combined temperature and moisture effects on PBO fibers,⁷ changes in the chemical, morphological, and mechanical properties were observed after exposure.

The chemical structure of poly(*p*-phenylene terephthalamide), commonly referred to as *polyaramid* or *aramid*, is shown in Figure 2. This material derives its strength from its highly crystalline structure, which contains intermolecular hydrogen bonds between the carbonyl groups and protons on neighboring polymer chains and the partial π stacking of the benzenoid aromatic structures between stacked strands. Aramid fiber is produced by solution spinning with a co-solvent with an ionic component (cal-

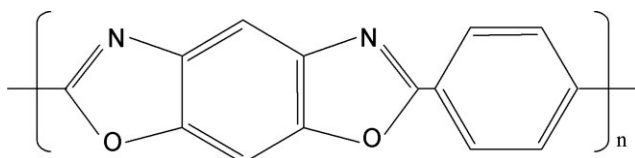


Figure 1 Chemical structure of PBO.

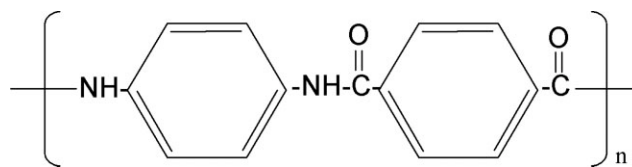


Figure 2 Chemical structure of poly(*p*-phenylene terephthalamide).

cium chloride) to occupy the hydrogen bonds of the amide groups and an organic solvent (*N*-methyl pyrrolinidone) to dissolve the aromatic polymer. The use of concentrated sulfuric acid in aramid production is required to keep the highly insoluble polymer in solution during synthesis and spinning.⁸

Although aramid fiber has neither the highest tensile strength nor the highest modulus among high-performance fibers, it offers a favorable balance of key properties, such as high tensile properties, light weight, chemical resistance, and thermal and dimensional stability. As with PBO, aramid fibers have relatively low axial and transverse compression properties and shear properties because of the anisotropic structure of the fibers. In general, aramid fibers are resistant to most organic solvents but are susceptible to attack by strong bases or acids at elevated temperatures or high concentrations. Aramid fibers are hydrolyzed under certain conditions but at a negligible rate under ambient conditions (nominally, 23°C and 15% relative humidity).⁸

The chemical structure of UHMWPE, also known as high-modulus polyethylene or high-performance polyethylene, is shown in Figure 3. UHMWPE fiber is a thermoplastic material that is highly resistant to corrosive chemicals, with the exception of oxidizing acids. UHMWPE fibers are produced by a gel-spinning process with a 1–5 mass % solution of polyethylene in paraffin oil.⁹ Despite the relatively weak van der Waal's forces between the chains, UHMWPE fiber derives substantial strength from the length of the individual polymer molecules and their high degree of alignment. As shown in Figure 3, the simple, nonpolar structure of the molecule also gives rise to surface and chemical properties that are rare in high-performance polymers. Because these fibers do not contain polar chemical groups

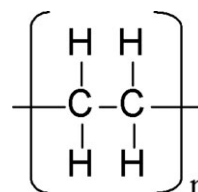


Figure 3 Chemical structure of UHMWPE.

(e.g., esters, amides, hydroxyls) that are susceptible to chemical and/or hydrolytic attack, they are very resistant to water, moisture, most chemicals, UV radiation, and microorganisms.

EXPERIMENTAL

Materials

The types and properties of the commercially available ballistic materials used in this study are listed as follows:

- Virgin aramid yarn, 167 tex.
- Plain-weave scoured aramid fabric constructed from 167-tex aramid warp and fill yarns, areal density = 332 g/m², no surface treatment.
- Plain-weave water-repellent-treated (WRT) aramid fabric constructed from 167-tex aramid warp and fill yarns, areal density = 332 g/m², treated with a water-repellent finish.
- Virgin UHMWPE yarn, 150 tex.
- Virgin PBO yarn, 55 tex.

Artificial perspiration

The composition of human perspiration depends on age, ethnicity, metabolism, and level of activity; thus, it is difficult to define a standard formulation for artificial perspiration. Although human perspiration is composed of 99% water, it also contains NaCl, KCl, urea, NH₄Cl, lactic acid, and acetic acid. Table II compares the composition of natural perspiration^{10,11} to artificial perspiration solutions.^{12,13} For this study, the perspiration solution recipe in ISO 3160-2¹² was selected. The pH of the artificial perspiration solution did not change significantly after 59 immersion cycles, as shown in Table III. The immersion of the ballistic materials was also carried out in plain distilled water to clearly separate hydrolytic degradation from the effects of the other components of artificial perspiration.

TABLE II
Chemical Composition of the Artificial Perspiration Solutions Compared to Human Perspiration

Component	Human perspiration ^{10,11}	ISO 3160-2 ¹²	EN 1811 ¹³
NaCl (g/L)	5.84–8.65	20	5
KCl (g/L)	0.067–1.012		
NH ₄ Cl (g/L)		17.5	
Urea (g/L)	0.768–3.420	5	1
Acetic acid (g/L)		2.5	1
Lactic acid (g/L)	0.60–3.60	15	
pH	4.0–6.8	Adjusted to 4.7 with NaOH	Adjusted to 6.6 with NH ₄ OH

TABLE III
pH Values for Artificial Perspiration, Cleaning Chemical Solutions, and Water Before and After 59 Immersion Cycles

	Initial pH	Final pH (after 59 cycles)
Water	7.43	7.34
Artificial perspiration	4.63	4.67
Bleach	10.62	8.83
Odor neutralizer	8.80	5.90
Detergent	8.64	8.5

Cleaning chemicals

Separate 5 mass % solutions in distilled water were prepared for a commercially available odor neutralizer, liquid detergent, and chlorine bleach. The primary ingredients in the odor neutralizer were listed as cyclodextrin (odor eliminator derived from corn), water, ethanol, fragrance, and unspecified quality control agents. The active ingredients in the liquid detergent were biodegradable surfactants (anionic and nonionic), ethanol, monoethanolamine, sodium tetraborate, and unspecified enzymes. The chlorine bleach was a 6% sodium hypochlorite solution in water and also contained some unspecified ingredients. The solution pH values before and after 59 immersion cycles are shown in Table III. The pH of the bleach solution decreased from 10.62 to 8.826; this was attributed to the loss of chlorine from the solution during the exposure period. The odor neutralizer solution pH was also observed to decrease from 8.80 to 5.90. The reason for this is unknown.

Perspiration and cleaning chemical exposure cycles

As shown in Figure 4, PBO, aramid, and UHMWPE yarns were wound on plastic dye tubes (Precision

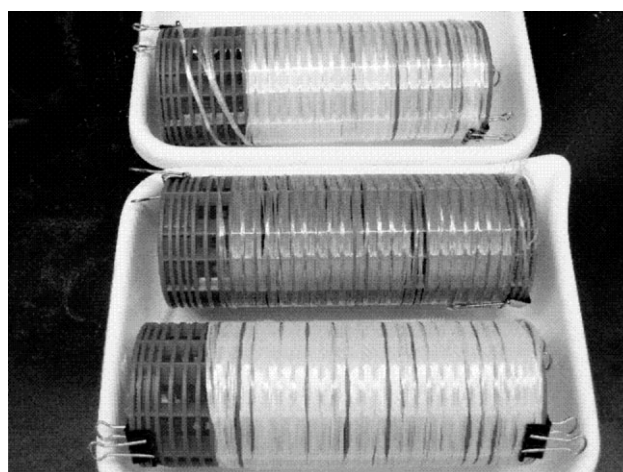


Figure 4 Yarns wound on dye tubes.

Spools, Inc., Pittsfield, MA) with a length of 170 mm and a diameter of 54 mm. Yarns were wound gently to minimize damage, which could result in a loss of mechanical properties. The yarn ends were secured to the dye tubes with metal binder clips covered with plastic bags to prevent corrosion.

The yarn tubes and fabric samples were fully immersed in the artificial perspiration solution and cleaning chemical solutions with using a cycle composed of 1 h of immersion at room temperature followed by 3–4 days in a 40°C oven. All analyses were carried out during the 40°C phase of the immersion cycle. Specimens underwent 59 immersion/drying cycles (ca. 9 months of total testing time). Because of the rapid deterioration of all materials exposed to the bleach solution, only 29 immersion/drying cycles (ca. 4 months) were used. For baseline measurements, one set of each material undergoing exposure was also cycled in plain distilled water, and one set was stored at 40°C.

Tensile testing

For tensile testing of the yarns, the appropriate lengths of yarn needed were measured and cut from the main spool at each inspection. For the fabric samples, individual yarns were extracted from the fabric for testing. To obtain the yarn mechanical properties, tensile testing of yarns in their dry state was carried out in accordance with ASTM D 2256-02 ("Standard Test Method for Tensile Properties of Yarn by the Single-Strand Method") with an Instron (Norwood, MA) model 4482 test frame equipped with a 91-kg (200-lb) load cell and pneumatic yarn and cord grips (Instron model 2714-006). The jaw separation was 7.9 cm (3.1 in.), and the crosshead speed was 2.3 cm/min (0.9 in./min). The yarns were nominally 6.3 cm (16 in.) long and were given 64 twists (4 twists/in.) on a custom designed yarn-twisting device. The twist value was calculated with the recommended calculation in section 10 of ASTM D 2256-02: $(110 \text{ twist/in.} \pm 10 \text{ twist/in.}) \times (\text{Denier})^{-1/2}$. This level of twist was maintained on the yarns as they were inserted into the pneumatic yarn and chord grips. A minimum of 10 replicates was tested to failure. The standard uncertainty of these measurements was typically $\pm 5\%$. After each set of tests, a 25-cm length of yarn was stored for potential future analyses.

Infrared analysis

Infrared analysis was carried out with a Nicolet (Waltham, MA) Nexus Fourier transform infrared (FTIR) spectrometer equipped with a mercury cadmium telluride detector and a SensIR Durascope attenuated total reflectance accessory (Dansburg, CT). Consistent pressure on the yarns was applied

with the force monitor on the Durascope. Dry air was used as the purge gas. FTIR spectra were recorded at three different locations on each yarn and were averaged over 128 scans. Spectral analysis, including spectral subtraction, was carried out with a custom software program developed in the Polymeric Materials Group at the National Institute of Standards and Technology (NIST) to catalog and analyze multiple spectra.¹⁴ The spectra were baseline-corrected and normalized with the aromatic C–H deformation peak at 848 cm^{-1} for PBO, the aliphatic C–H bend at 1472 cm^{-1} for UHMWPE, and the aromatic deformation peak at 820 cm^{-1} for aramid. We carried out spectral subtraction by subtracting the baseline (unexposed) spectra from the spectra of the exposed materials. The standard uncertainties associated with this measurement were $\pm 4 \text{ cm}^{-1}$ in wave number and $\pm 1\%$ in absorbance.

Laser scanning confocal microscopy

A Zeiss model LSM510 reflection laser scanning confocal microscope was used to qualitatively characterize the fiber surface morphology. The incident laser wavelength was 543 nm. When the focal plane is moved in the z direction, a series of single images (optical slices) can be stacked and digitally summed over the z direction to obtain a three-dimensional image. The z -direction step size was $0.5 \mu\text{m}$ with objectives of $5\times$ and $10\times$ and $0.1 \mu\text{m}$ with objectives of $20\times$, $50\times$, and $150\times$. At a magnification of $150\times$, the dimensions of each image were $61.4 \times 61.4 \mu\text{m}^2$ (512×512 square pixels).

RESULTS AND DISCUSSION

Tensile properties

The tensile properties of ballistic fibers are critical to the ballistic performance of soft body armor.¹ The changes in the tensile strength, elongation at break, and tensile modulus are shown as a function of immersion cycle in Figures 5–9. Table IV presents the percentage change in the yarn tensile properties after 29 cycles of immersion in bleach solution and 59 cycles in water artificial perspiration, odor neutralizer, and detergent solutions. The percentage change corresponds to

$$[(\text{Value}_{\text{final}} - \text{Value}_{\text{initial}})/\text{Value}_{\text{initial}}] \times 100$$

The stress–strain curves for the three materials were essentially studied up to the point of failure. To determine the statistical significance of the observed changes in the tensile properties relative to the baseline, a two-population t test¹⁵ at a 95% confidence level was applied to the data. Additionally,

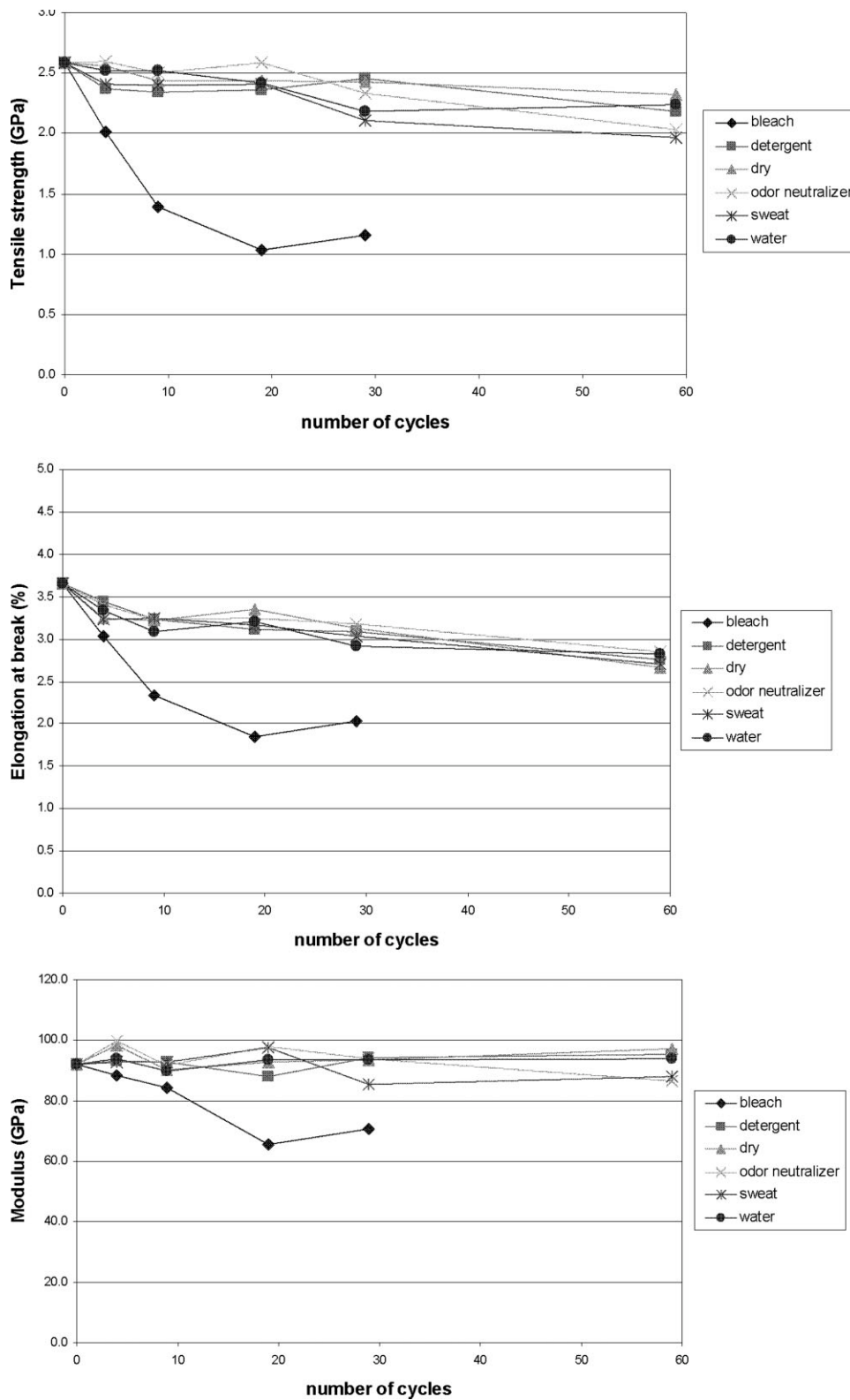


Figure 5 Changes in the tensile strength, elongation at break, and modulus of aramid yarn as a function of artificial perspiration and cleaning chemical immersion. The standard uncertainty of these measurements was typically $\pm 5\%$.

to determine the statistical significance of the observed changes in the tensile properties after artificial perspiration and cleaning chemical exposure

relative to the changes in the tensile properties after plain water exposure, a two-population *t* test at a 95% confidence level was applied to the data.

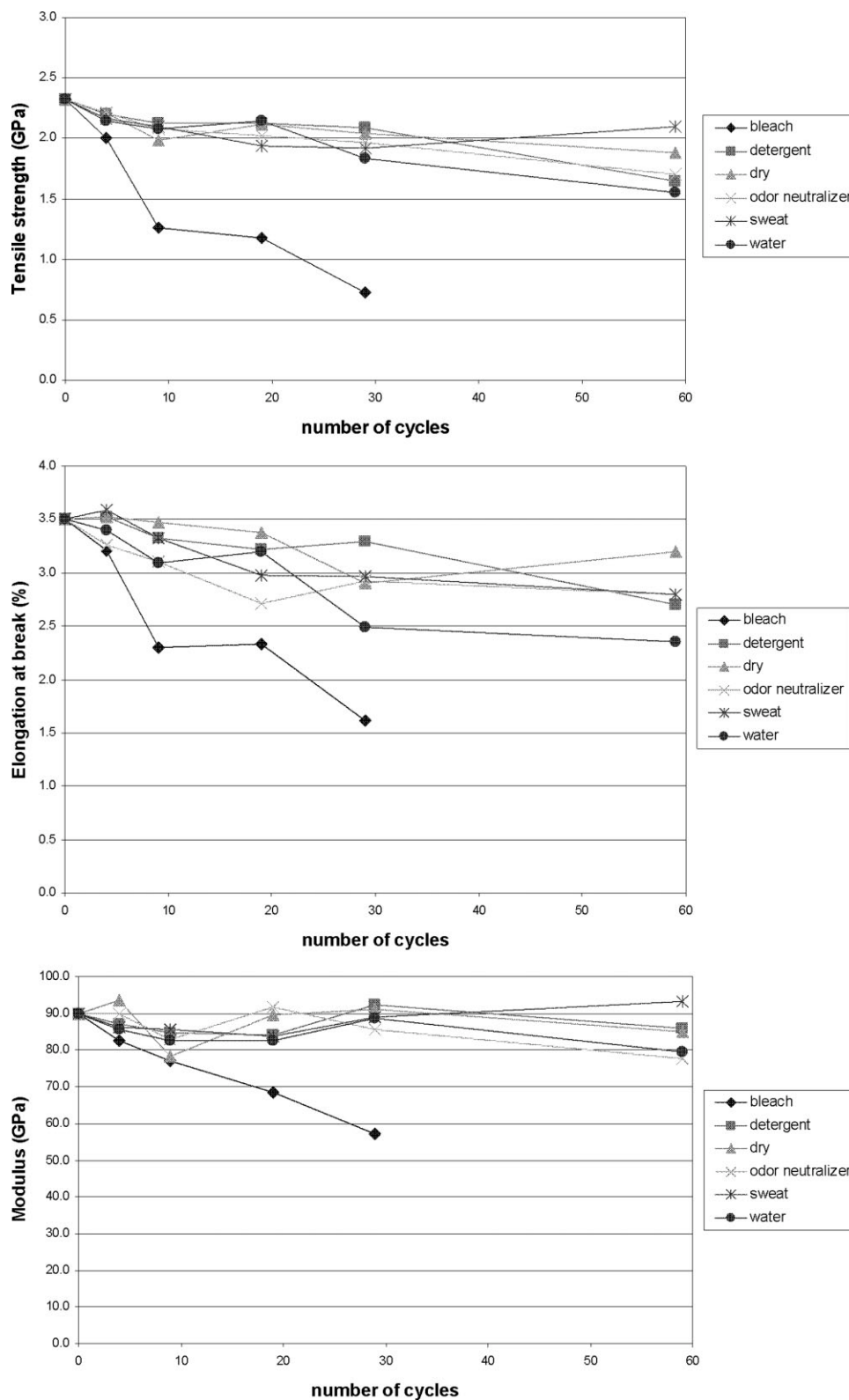


Figure 6 Changes in the tensile strength, elongation at break, and modulus of yarns extracted from scoured aramid fabric as a function of artificial perspiration and cleaning chemical immersion. The standard uncertainty of these measurements was typically $\pm 5\%$.

Before we discuss the tensile data, we must note that slippage of the UHMWPE yarns initially occurred when we used grips with a 1.75-kN

capacity. This was particularly problematic for UHMWPE fibers immersed in the detergent solution, and specimens that slipped in the grips were not

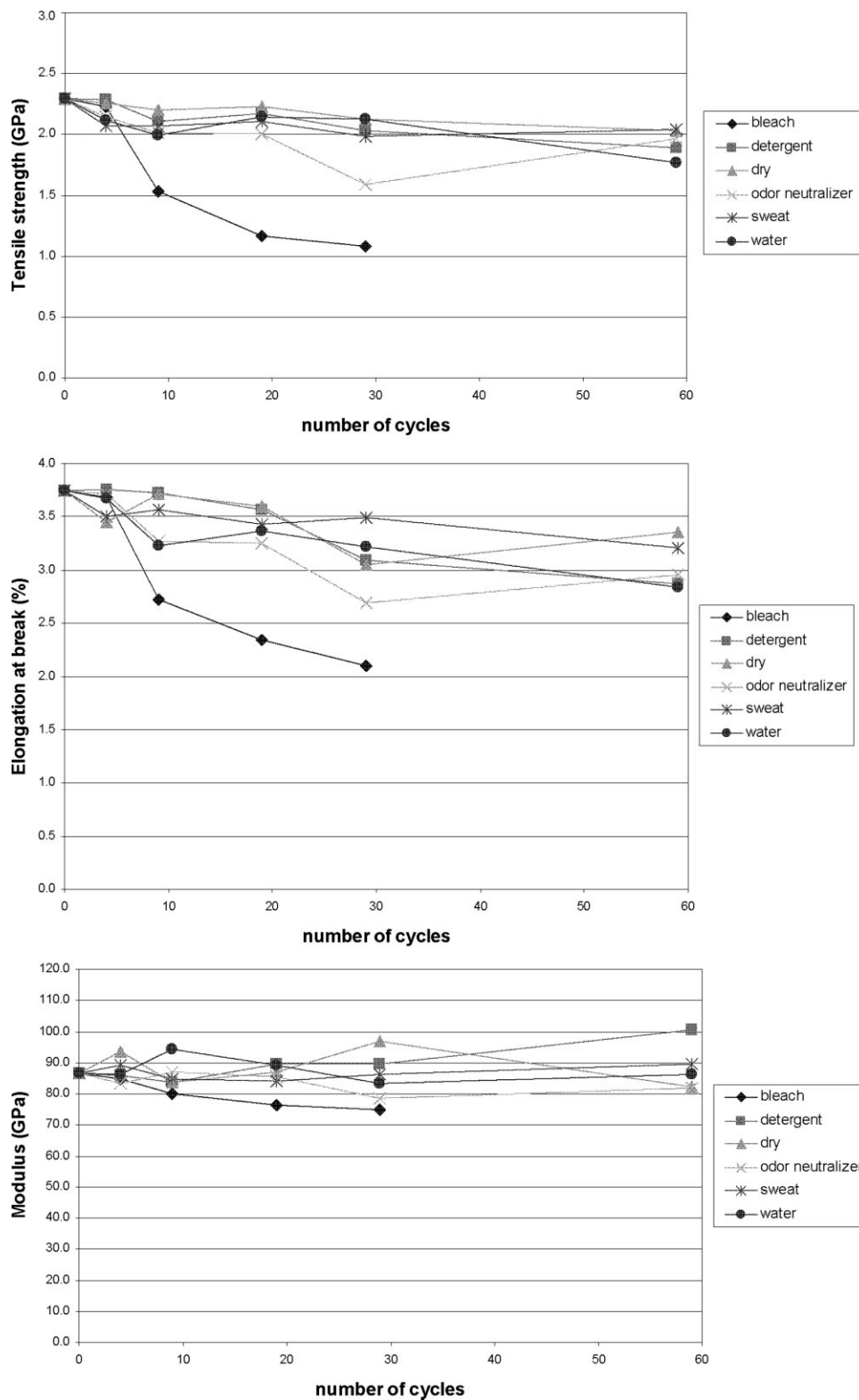


Figure 7 Changes in the tensile strength, elongation at break, and modulus of yarns extracted from WRT aramid fabric as a function of artificial perspiration and cleaning chemical immersion. The standard uncertainty of these measurements was typically $\pm 5\%$.

used in the calculation of the tensile properties. In subsequent testing of UHMWPE, we found that the use of 2.0-kN grips alleviated this problem.

In the evaluation of the effects of the exposure conditions on fiber properties, all immersion environments were aqueous in nature, so any observed

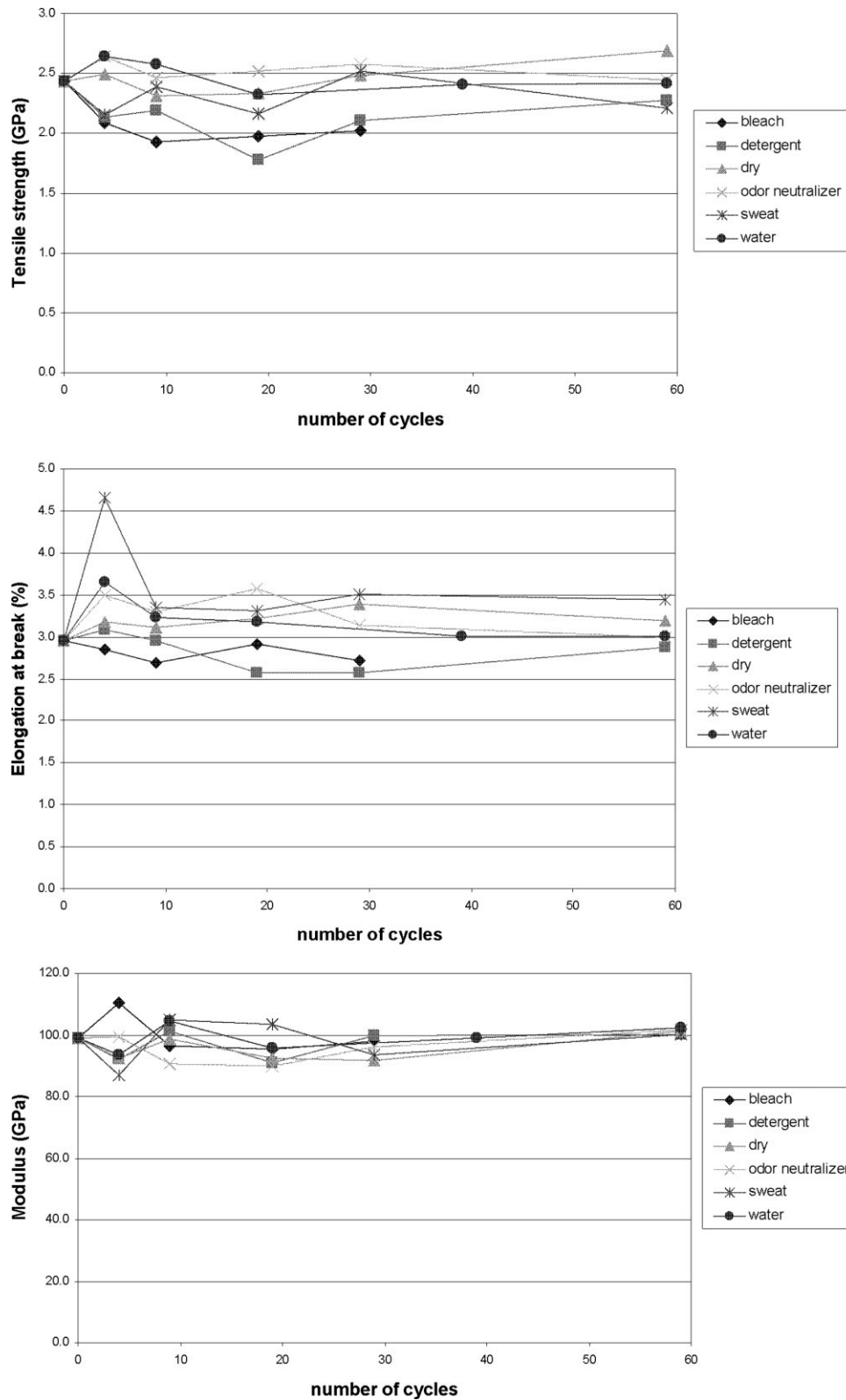


Figure 8 Changes in the tensile strength, elongation at break, and modulus of UHMWPE yarns as a function of artificial perspiration and cleaning chemical immersion. The standard uncertainty of these measurements was typically $\pm 5\%$.

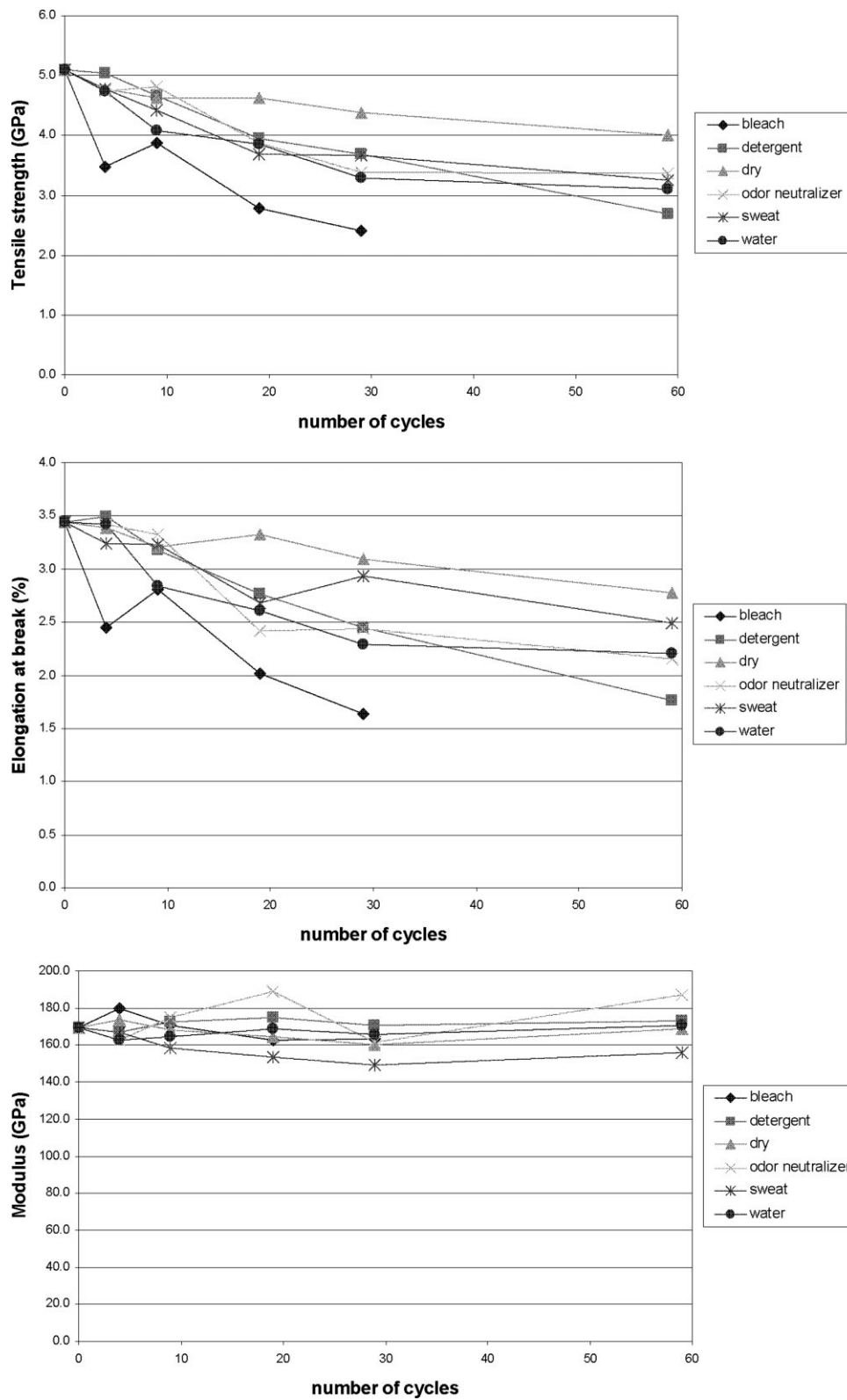


Figure 9 Changes in the tensile strength, elongation at break, and modulus of PBO yarns as a function of artificial perspiration and cleaning chemical immersion. The standard uncertainty of these measurements was typically $\pm 5\%$.

effects would also include the contribution of water. Both the aramids and PBO are known to be susceptible to hydrolysis^{16,17} and exhibited decreases in the tensile properties after water exposure in this study.

Because UHMWPE is nonpolar, decreases in the tensile properties after water exposure were not observed.

It is puzzling why the fibers that were continuously stored at 40°C during the study also exhibited

TABLE IV
Percentage Changes in the Tensile Properties of the Ballistic Fibers After Artificial Perspiration and Cleaning Chemical Exposure Relative to the Baseline Properties

	Dry			Water			Artificial perspiration			Odor neutralizer			Bleach			Detergent		
	σ_{\max}	ϵ_{\max}	E_{young}	σ_{\max}	ϵ_{\max}	E_{young}	σ_{\max}	ϵ_{\max}	E_{young}	σ_{\max}	ϵ_{\max}	E_{young}	σ_{\max}	ϵ_{\max}	E_{young}	σ_{\max}	ϵ_{\max}	E_{young}
Aramid yarn	-10.18 ^a	-27.15 ^a	5.59	-13.67 ^a	-22.96 ^a	2.01	-24.07 ^a	-26.26 ^a	-4.60	-21.70 ^a	-22.13 ^a	-6.36	-60.12 ^a	-49.48 ^a	-28.93 ^a	-15.66 ^a	-24.68 ^a	3.58
Scoured aramid fabric	-19.01 ^a	-8.71	-5.33	-33.18 ^a	-32.84 ^a	-1.22	-9.61 ^a	-20.25 ^a	3.75	-26.53	-20.30 ^a	-13.49	-49.54 ^a	-33.57 ^a	-23.79 ^a	-29.23 ^a	-23.06 ^a	-4.42
WRT aramid fabric	-11.71	-10.53	-4.99	-23.15 ^a	-24.35 ^a	-0.22	-11.06	-14.44	3.37	-14.40	-21.18 ^a	-5.43	-49.07 ^a	-35.53 ^a	-14.70	-17.80 ^a	-23.32 ^a	15.95
PBO	-21.22 ^a	-19.39 ^a	-0.14	-39.07 ^a	-35.99 ^a	0.84	-36.20 ^a	-27.62 ^a	-7.81 ^a	-34.09 ^a	-37.45 ^a	10.49	-45.68 ^a	-40.15 ^a	-10.10	-47.40 ^a	-48.69 ^a	2.45
UHMWPE	10.50	7.74	2.32	-0.56	1.56	3.38	-9.19	8.22	0.94	0.49	1.01	2.47	-18.81 ^a	-1.39	-3.90	-6.34	-2.79	1.01

^a Statistically significant.

σ_{\max} , tensile strength at break; ϵ_{\max} , strain at break; E_{Young} , Young's modulus.

changes in the tensile properties. We speculate that, because all of the materials were stored in the same 40°C oven, the local relative humidity in the oven was raised for a short period of time each time the wet specimens were replaced after the aqueous immersion portion of the cycle. This repeated, short-term exposure to elevated relative humidity may have contributed to the decreases in the tensile properties observed for this set of materials. Thus, no conclusion could be drawn as to whether or not the 40°C drying step alone contributed to any observed deterioration in the tensile properties.

In general, the organic and inorganic compounds in the artificial perspiration solution, detergent, or odor neutralizer did not appear to play a statistically significant role in additional fiber degradation beyond that of water alone, as determined by the two-population *t* test with a confidence interval of 95%. The only exception was that of virgin aramid yarn, which exhibited decreases in the tensile properties after exposure to the artificial perspiration and odor neutralizer solutions beyond that induced by water.

After 29 bleach solution exposure cycles, all materials exhibited substantial decreases in the tensile strength, elongation at break, and tensile modulus that were statistically different from changes produced by plain water, as determined by the *t* test. Commercial chlorine bleach is essentially an aqueous solution of sodium hypochlorite, which is a strong oxidizer. In water, sodium hypochlorite hydrolyzes into sodium hydroxide and hypochlorous acid. Both compounds are known to contribute to the hydrolysis of PBO and aramid-based materials.^{6,8}

Relative to the baseline values, decreases in the tensile strength after bleach solution exposure were 19% for UHMWPE, between 50 and 60% for the various aramids, and 45% for PBO. The elongation at break after bleach exposure was unchanged for UHMWPE, but decreases in elongation at break were observed for both the aramids (33–49%) and PBO (40%). Changes in the tensile modulus induced by the bleach solution were minimal for UHMWPE but were substantial for the aramids (15–29%) and PBO (10%). In Ref. 6, a 48% loss in the tensile strength of PBO was reported after a 100-day exposure to hypochlorite bleach solution.

A comparison of the yarns extracted from the scoured and WRT fabrics to the virgin aramid yarn revealed that, with the exception of the bleach exposure, the WRT fabric exhibited a smaller degree of loss in properties than its scoured counterpart. We speculate that the water-repellent treatment on the fiber was compromised by the bleach solution, but it did serve to partially protect the fabric from the effect of the various solutions.

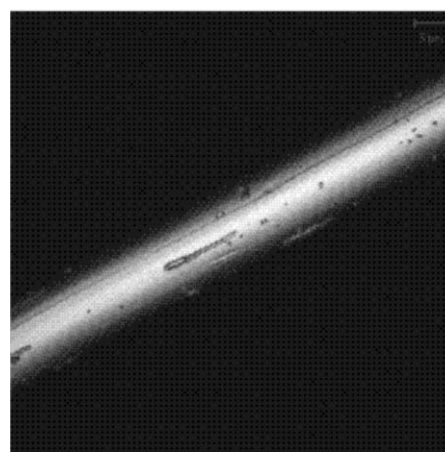
We also hypothesize that, in a woven fabric, the properties of the individual yarns are affected by the weaving operation and are, in turn, affected more by their external environment. However, there were no clear trends observed in the behavior of the yarns extracted from the aramid fabrics compared to the aramid yarn.

Surface morphology

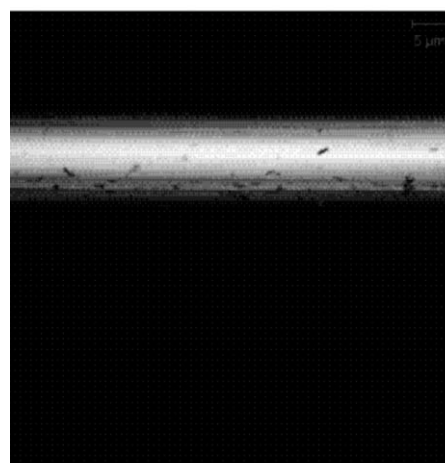
Confocal microscopy was carried out to visually and qualitatively assess changes in the fiber surface morphology. Representative confocal images showing the fibers before immersion, after 29 cycles of water immersion, and after 29 cycles of bleach solution immersion are shown in Figures 10–14. After 29 cycles of bleach immersion, significant pitting was observed on all of the fiber surfaces. The surface morphology of the water-exposed aramids and UHMWPE (shown in Figs. 10–12 and 13, respectively) was unchanged relative to the unexposed specimens. This indicated that the surface morphology changes observed in the bleach-exposed fibers were due to the oxidizers in the bleach solution and not to water exposure. In the PBO confocal micrographs shown in Figure 14, differences in the surface morphology are evident between the unexposed fibers and both the water-exposed and bleach exposed fibers. Very little difference in the surface appearance was observed between the water-exposed fibers and the bleach-exposed fibers. However, because the tensile properties of the bleach-exposed yarns were more highly degraded than those of the water-exposed yarns, we speculate that the damage initiated by the bleach exposure penetrated deeper into the bulk of the fiber.

Chemical structure

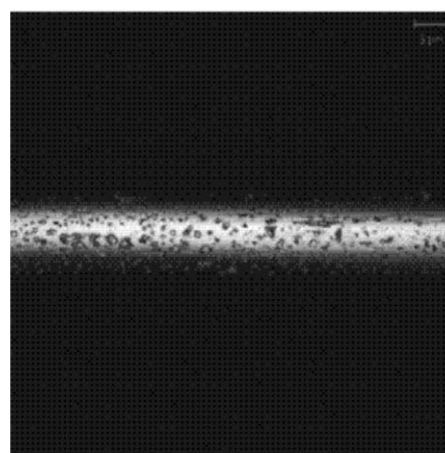
Changes in the intensities or frequencies of observed infrared spectral peaks can be correlated to changes in the molecular structure of a compound. Spectral subtraction, in which a reference spectrum is subtracted from the spectrum of a material of interest, is helpful in the extraction of small chemical changes and for providing information on the formation and depletion of specific functional groups. In addition to the references given, peak assignments were made with the guidance of ref. 16. In the difference spectra presented in this section, downward-pointing, or negative, peaks are species that were lower in concentration relative to the reference spectrum (unexposed materials, in this case), and upward-pointing, or positive, peaks are species that were higher in concentration relative to the reference material or new species that were not originally present in the reference material.



(a)



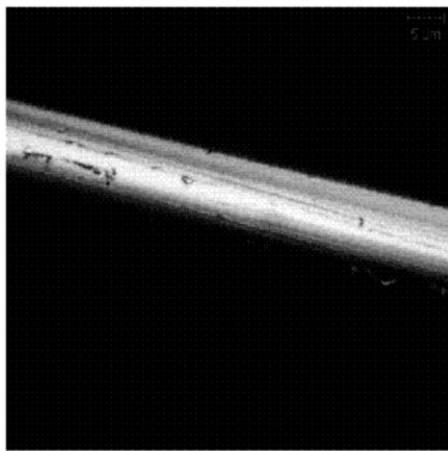
(b)



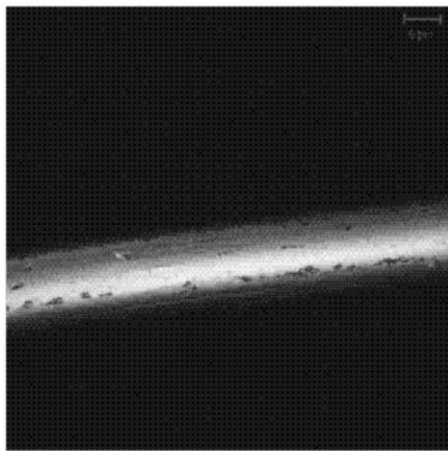
(c)

Figure 10 Representative confocal microscope images of aramid fibers (a) before exposure, (b) after 29 cycles of water exposure, and (c) after 29 cycles of bleach solution exposure.

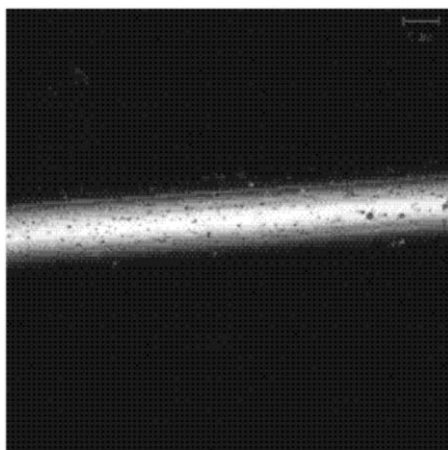
All aramid and PBO spectra showed evidence of hydrolytic degradation, and no UHMWPE spectra showed any significant chemical changes with the exception of the bleach-immersed specimens. In the



(a)



(b)

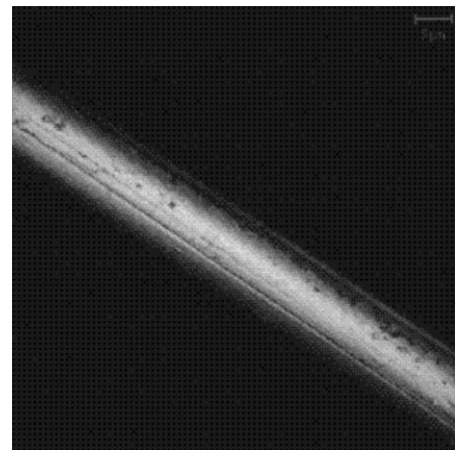


(c)

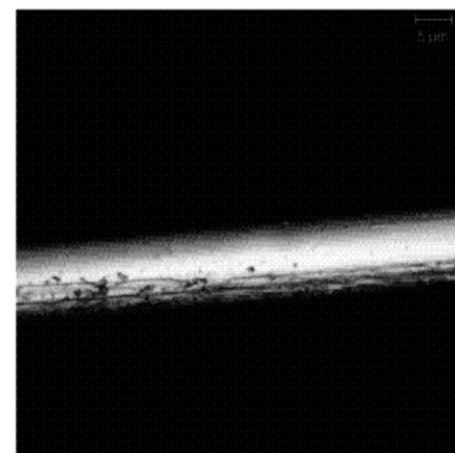
Figure 11 Representative confocal microscope images of fibers extracted from scoured aramid fabric (a) before exposure, (b) after 29 cycles of water exposure, and (c) after 29 cycles of bleach solution exposure.

interest of space, spectra are shown here only for specimens after bleach solution immersion, as these specimens exhibited the largest degree of tensile strength loss.

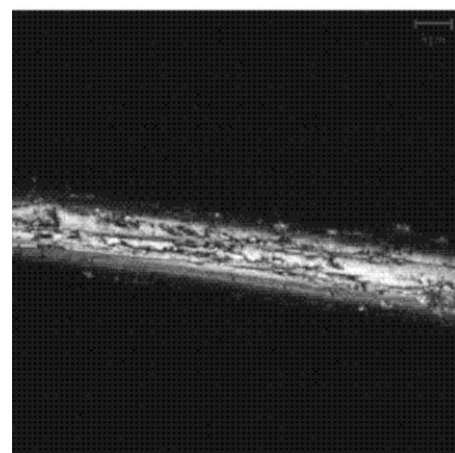
The infrared spectrum of aramid yarn and the resulting difference spectrum after bleach exposure is shown in Figure 15(a,b). Results for the scoured and WRT aramid fabrics were very similar and are



(a)

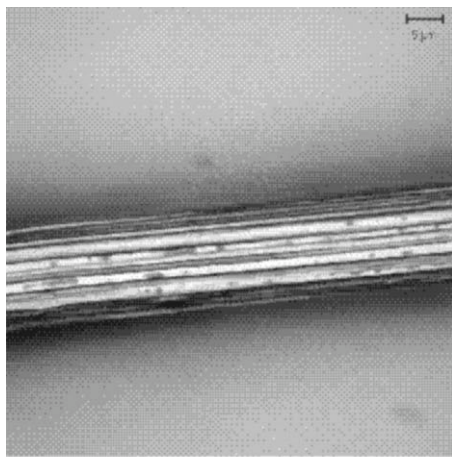


(b)

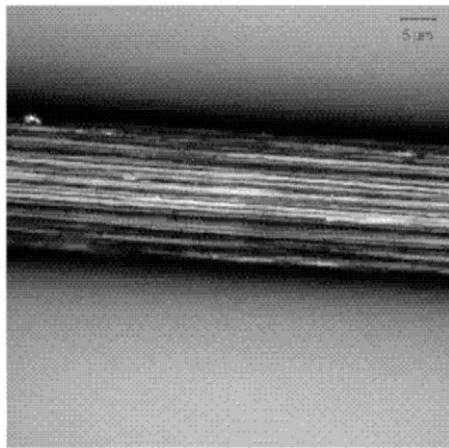


(c)

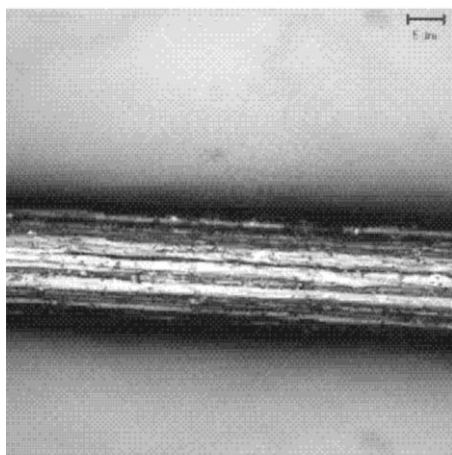
Figure 12 Representative confocal microscope images of fibers extracted from WRT aramid fabric (a) before exposure, (b) after 29 cycles of water exposure, and (c) after 29 cycles of bleach solution exposure.



(a)



(b)

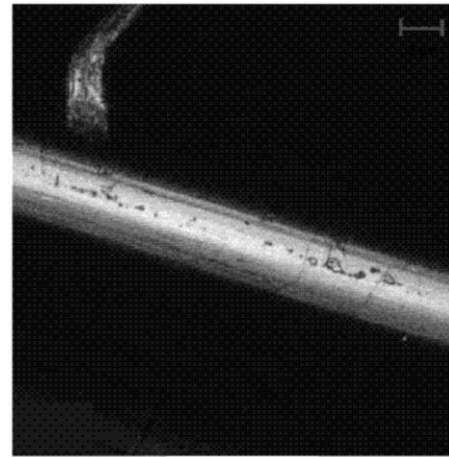


(c)

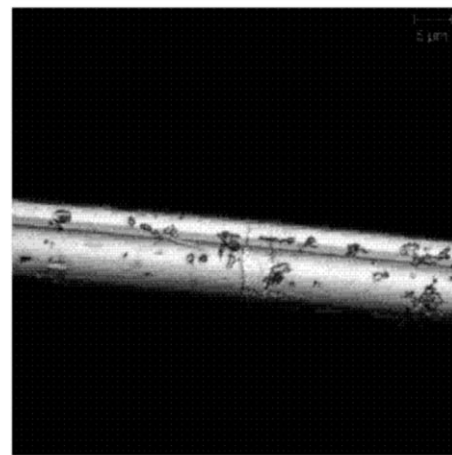
Figure 13 Representative confocal microscope images of UHMWPE fibers (a) before exposure, (b) after 29 cycles of water exposure, and (c) after 29 cycles of bleach solution exposure.

not shown here. As shown in Figure 15(a), characteristic infrared peaks for aramids are the amide N—H stretching at 3320 cm^{-1} , carbonyl stretching at 1640

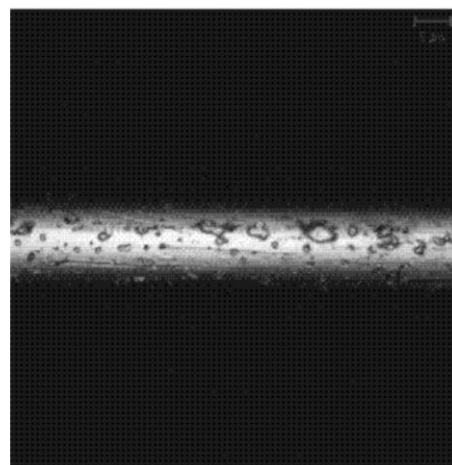
cm^{-1} (amide I), N—H bending/C—N stretching interactions at 1535 and 1513 cm^{-1} (amide II), and C—N stretching at 1305 cm^{-1} .^{18,19} The difference



(a)



(b)



(c)

Figure 14 Representative confocal microscope images of PBO fibers (a) before exposure, (b) after 29 cycles of water exposure, and (c) after 29 cycles of bleach solution exposure.

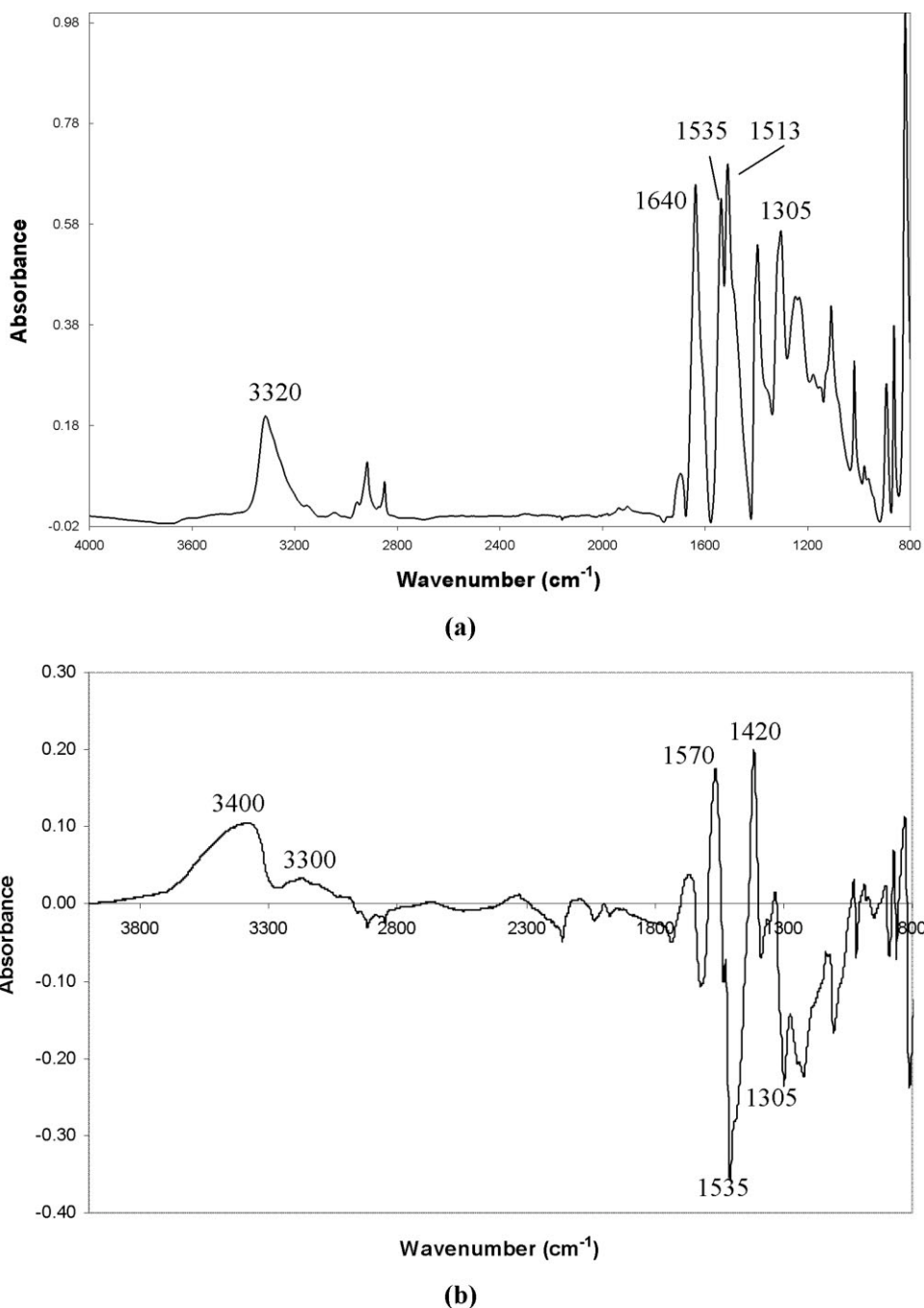
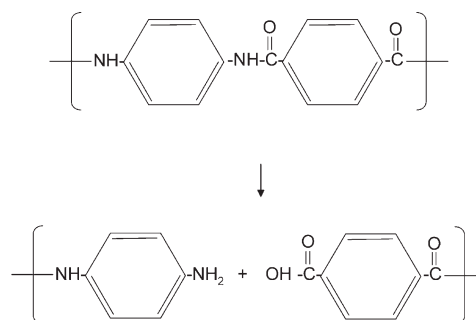


Figure 15 (a) FTIR spectrum of unexposed aramid yarns and (b) difference spectrum of aramid yarns after 29 cycles of bleach solution exposure referenced to the spectrum of unexposed yarns.

spectrum in Figure 15(b) shows new broad peaks centered at 3400 and 3200 cm^{-1} , which were attributed to a combination of amine N–H stretching and carboxylic acid OH stretching. New peaks were also observed at 1570 and 1420 cm^{-1} , which were attributed to carboxylate ion stretching. Negative peaks with positions corresponding to the original amide I, amide II, and C–N stretching peaks were also observed. This evidence pointed to the hydrolysis of the main-chain amide group to amine and carboxylic acid¹⁶:



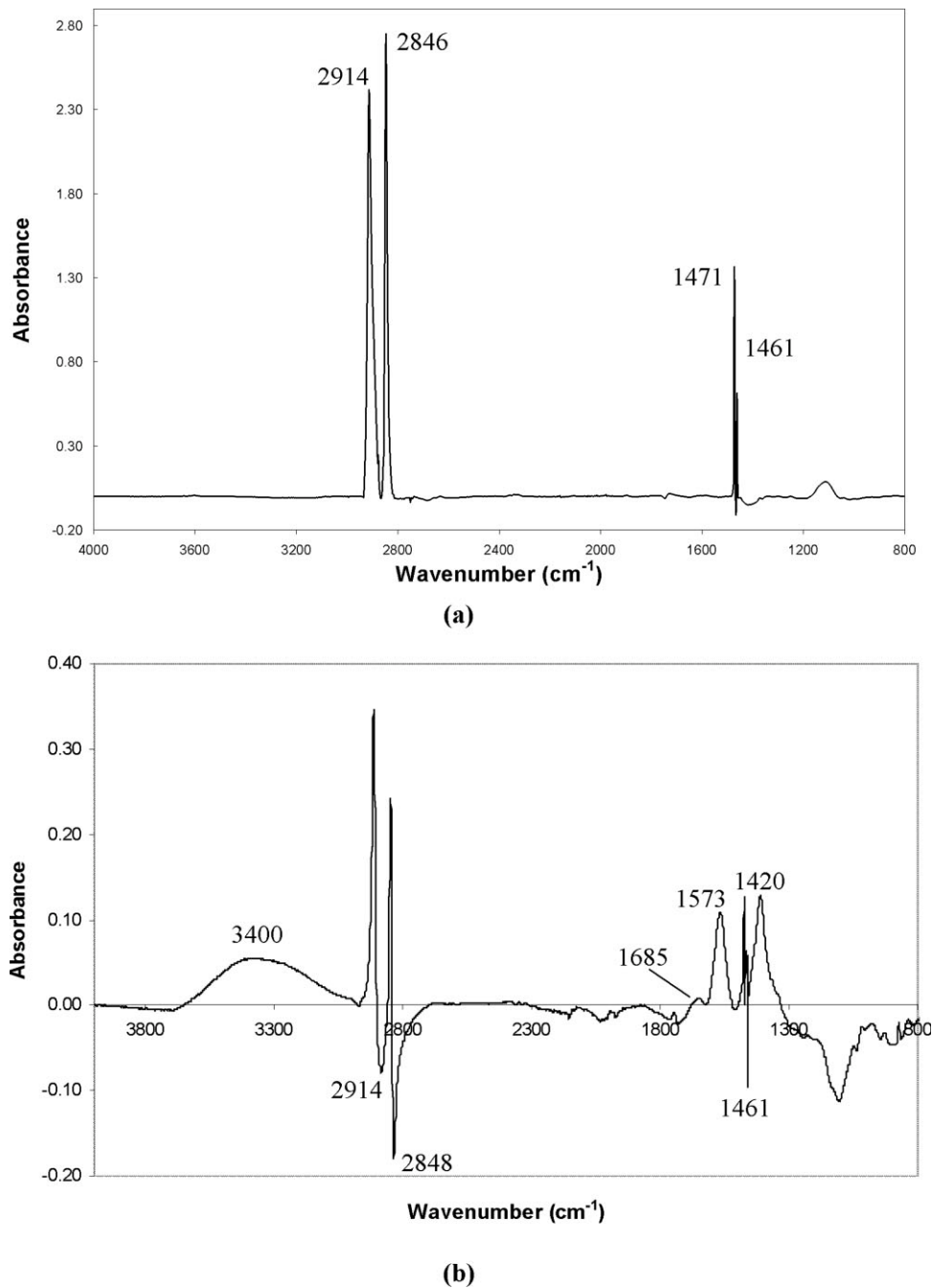


Figure 16 (a) Spectrum of unexposed UHMWPE yarns and (b) difference spectrum of UHMWPE yarns after 29 cycles of bleach solution exposure referenced to the spectrum of unexposed yarns.

This degradation mode resulted in chain scission and a subsequent loss of tensile properties.

The spectrum of UHMWPE and the resulting difference spectrum after bleach exposure are shown in Figure 16(a,b). Figure 16(a) shows the characteristic peaks for UHMWPE, identified as C–H stretching at 2914 and 2846 cm⁻¹ and C–H bending at 1470 and 1461 cm⁻¹. The difference spectrum in Figure 16(b) shows new peaks at 3400 cm⁻¹ (broad), attributed to O–H stretching from an oxidized species, and at

1573 and 1420 cm⁻¹, characteristic of carboxylate ion stretching. Negative peaks corresponding to the original C–H stretching peaks at 2914 and 2846 cm⁻¹ were also observed, which indicated a change in the original polyethylene structure. Similar changes in chemical structure have been observed for polyethylene exposed to oxidizing conditions, which cause chain scission or crosslinking of the polyethylene chains and lead to the degradation of polyethylene's mechanical properties.^{20,21}

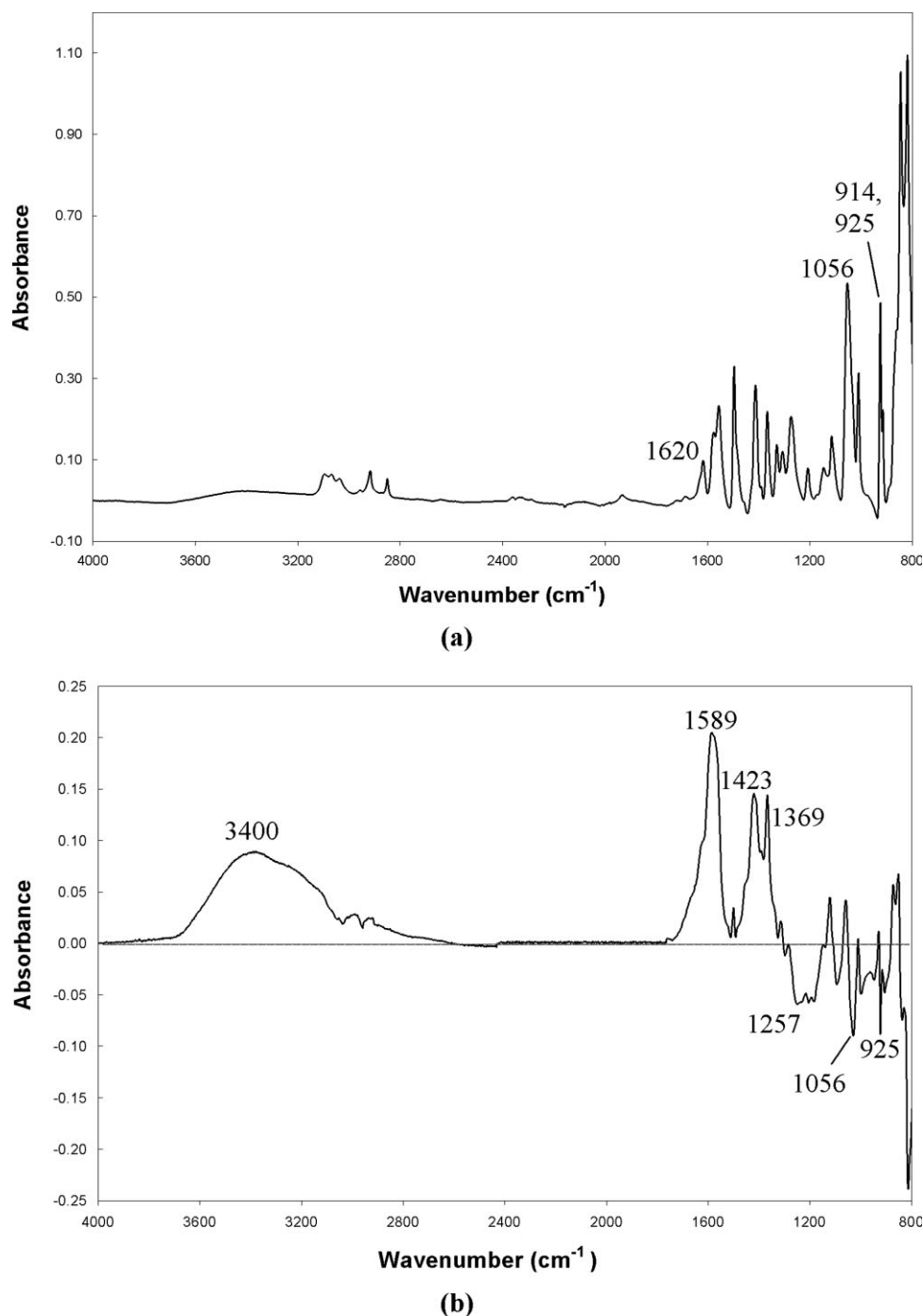
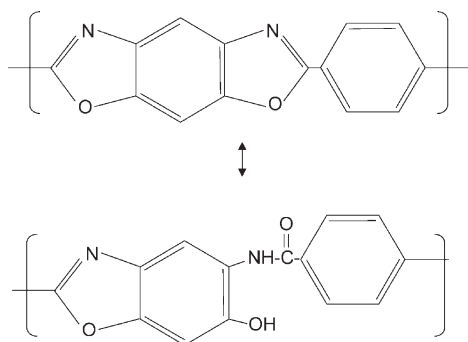


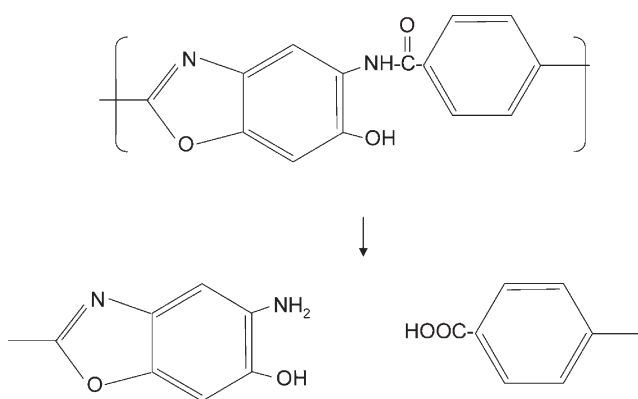
Figure 17 (a) Spectrum of unexposed PBO yarns and (b) difference spectrum of PBO yarns after 29 cycles of bleach solution exposure referenced to the spectrum of unexposed yarns.

In the spectrum of PBO shown in Figure 17(a), the peaks at 1620, 1056, 925, and 914 cm⁻¹ were identified as stretching modes associated with the benzoxazole ring, which is the most prominent chemical feature of PBO.²² After bleach exposure, the difference spectrum in Figure 17(b) reveals a broad new peak centered at 3400 cm⁻¹, which was a complex combination of amine N–H stretching and O–H stretching from carboxylic acids or phe-

nols, and peaks at 1589, 1423, and 1369 cm⁻¹, which were collectively attributed to carboxylate ion stretching and/or carboxylic acid C–O stretching and O–H bending. Negative peaks were found at 1056 and 925 cm⁻¹, which are the peak positions associated with the benzoxazole ring. This evidence provided support for a degradation mechanism that involves hydrolysis of the benzoxazole ring to benzamide.



and subsequently to aminophenol and carboxylic acid



Similar observations have been made by other researchers in the study of PBO hydrolysis.^{17,23}

CONCLUSIONS

The effects of perspiration and cleaning chemicals (odor neutralizer, solution, liquid detergent solution, and chlorine bleach) on the tensile, chemical, and surface morphological properties of aramid yarns and fabrics, UHMWPE yarn, and PBO yarn were investigated with controlled immersion/drying cycles.

The tensile properties of the aramid and PBO materials decreased after exposure to plain water, artificial perspiration, detergent, odor neutralizer, and chlorine bleach. The hydrophobic UHMWPE exhibited tensile strength decreases only in chlorine bleach. No degradation of the tensile properties beyond that induced by plain water was observed after artificial perspiration exposure for any of the ballistic materials. For all materials, only chlorine bleach caused a significant decrease in the tensile properties beyond that of plain water.

The analysis of the fiber surface morphology after exposure revealed that chlorine bleach caused physical changes in the fiber surfaces, which were primarily observed as small pits. These surface changes were not observed after exposure in water, with the

exception of PBO, in which the surface morphological changes induced by water and the bleach solution were roughly the same.

The chemical analysis of the bleach-exposed fibers via FTIR revealed significant chemical changes initiated by the strong oxidizers in bleach. Hydrolytic degradation was observed for the aramids and PBO, and evidence for oxidative degradation was observed for UHMWPE. Each of these damage modes could be correlated to the observed changes in the fiber tensile properties.

The results of this limited study show that chlorine bleach exposure over a period of time could be potentially damaging to soft body armor constructed from commercial aramid, UHMWPE, and PBO fibers and should be avoided in the routine care and cleaning of armor. Although exposure to aqueous-based cleaning and artificial perspiration solutions did not cause additional damage to ballistic fibers beyond that of water alone, it should still be noted that water did degrade the long-term mechanical properties of aramid and PBO fibers. Therefore, we recommend that the use of water and/or any aqueous-based products should be avoided or minimized in the care of soft body armor.

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