Influence of Finish Treatment on the Durability of Aramid Fibers Aged Under an Alkaline Environment

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ABSTRACT: Aramid fibers are high-performance materials which have been used in ropes and protective clothing for many years. They are also now being proposed in geotextiles for ground reinforcement. The influence of the surface finish composition and content has been studied in the field of cables and textiles, but there is no published data concerning the effect of a finish treatment on the hydrolytic degradation. Aramid fibers with different finish contents have been aged in an alkaline environment. The degradation has been identified by FTIR, viscosimetry, TGA, SEM, and tensile tests. For Technora fibers, the presence of finish appears to limit the tensile strength loss of aramid fibers at pH 11 by limiting abrasion, as well as bulk and surface degradation. For Twaron fibers, higher finish content only has a slight influence on the fibers durability at pH 11 and pH 9, by limiting abrasion and bulk degradation. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 888–898, 2010

Key words: aramids; fibers; aging; finish; hydrolysis

INTRODUCTION

A few years ago, geotextiles based on polyethylene terephtalate fibers were commonly used for alkaline ground reinforcement applications. However, when they were observed to display premature aging under these conditions (lime, cement, or slag treated soils, next to the skin of hardened concrete, etc.),[1] alternative solutions were developed, among which are geotextiles made of aramid fibers.[2,3] Two types of aramid material are considered here: Twaron fibers, based on poly(*p*-phenylene terephtalamide) (PPTA) similar to Kevlar fibers, and Technora fibers, based on copoly-(paraphenylene/3,4′-oxydiphenylene terephtalamide) (Fig. 1).

Twaron and Technora fibers both contain amide functions that are sensitive to hydrolysis[4,5]; although, Imuro and Yoshida[6] reported that the dilution of aramid-linkages by ether-linkages as in Technora fibers may contribute to provide the latter with better hydrolytic stability. The mechanism of PPTA hydrolysis has been identified and involves scission of the amide N—C linkage, yielding acid and amine functions[4,5] (Fig. 2).

Springer et al.[7] evaluated the influence of basic and acid hydrolytic treatments on the mechanical properties of PPTA fibers. They showed that both modulus and tensile strength were affected, but the property drops were larger in acid and basic solutions than in a neutral environment.

The processing of polymeric fibers generally includes a finish application step to improve their durability, performance, and/or processability. The finish formulations are varied and depend on the applications: they can be composed of lubricants (to prevent yarn abrasion), antistatics (to avoid yarn decohesion and facilitate their winding), emulsifiers, antioxidants, antimicrobial additives, etc.[8] The influence of the finish composition and content on the bending fatigue life of cables[9] and on the processing of nonwoven fabrics[10] have been studied. For instance, Moraes D'Almeida et al.[9] showed the bending fatigue life of Kevlar 29 braids is improved by a factor of four after impregnation in a polyurethane resin (4 wt %) that limits internal abrasion. In a similar way, Wagner and Ahles[10] highlighted that the addition of an antistatic and lubrication oil overlaid on Kevlar fibers improves the processing of nonwoven fabrics. However, the influence of the finish on the hydrolytic degradation of aramid fibers has not been discussed in detail previously.

In this article, the degradation of Twaron and Technora fibers with different finish contents in an alkaline environment has been evaluated and correlated with mechanical properties.

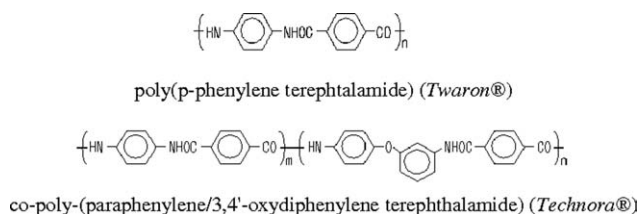*Correspondence to:* L. Vouyovitch Van Schoors (laetitia. van-schoors@lcpc.fr).

poly(p-phenylene terephtalamide) (*Twaron®*)

co-poly-(paraphenylene/3,4'-oxydiphenylene terephthalamide) (*Technora®*)

Figure 1 Aramid molecular structures.

EXPERIMENTAL

Materials

Two kinds of aramid fibers have been studied in this article: Twaron and Technora fibers, both produced by Teijin Aramid. The Twaron 1000 and Twaron 1010,in the form of 1680 dtex yarn, are based on the same polymer but have different finish contents: respectively 0.6–1 wt % and 0.14 wt %. In a similar way, Technora T240 and Technora T000 fibers, in the form of 1670 dtex yarns, are based on the same polymer but Technora T240 has 2.5 wt % of finish, whereas Technora T000 is finish free.

Aging methods

Yarn samples were immersed in buffer sodium carbonate salt solutions at pH 9 and pH 11 up to 1 year aging. Two temperatures have been considered for each aging condition: 20 and 80°C. Over the aging period considered here, the temperature variability is estimated at ± 2°C.

Analysis and characterization

Fourier transformed infrared (FTIR) was performed in Attenuated Total Reflectance mode (ATR) mode with a Nicolet impact 410 spectrometer and Durascope Diamond ATR equipment. The spectra were recorded with a resolution of 2 cm^{-1}, and an accumulation of 32 spectra. The spectra were analyzed with OMNIC 3.1 software. Each scan was made on a yarn, composed of 1000 filaments, and repeated three times per sample and condition.

Viscosity measurements were carried out using an Ubbelohde DIN (Schott Instruments) capillary viscosimeter, at 25°C. For Twaron fibers, the weight average molecular mass was calculated from the Mark-Houwink relationship established by Arpin and Stra-

zielle[11]: $\eta = 8 \times 10^{-3} M^{1.09}$. For that purpose, four concentrations between 5×10^{-4} g/mL and 2×10^{-3} g/mL were chosen. The reduced viscosity comparisons were performed at 2×10^{-3} g/mL. The fibers were beforehand dissolved in 50 mL of sulfuric acid concentrated at 96% for 2 h at 60°C with magnetic stirring. Above this dissolution temperature, additional degradation can occur in sulfuric acid.[12] For Technora fibers, the reduced viscosities measurements were conducted from three concentrations between 3×10^{-4} g/mL and 1.5×10^{-3} g/mL. The fibers were dissolved in 50 mL of sulfuric acid concentrated at 96% for 2 h at 60°C with magnetic stirring. Because of the presence of ether linkages, Technora fibers are more susceptible to strong acid exposure than are pure aramid Twaron fibers.[13] The remaining insoluble fractions after dissolution were extracted and weighed to calculate the true concentration of the solution.

Thermogravimetric analysis (TGA) continuously measures the mass of a sample subjected to a steady increase of temperature. The thermal analyzer used is a Netzsch STA 409 E. The data are processed with Proteus Analysis software. The temperature of the furnace was programmed to rise at constant heating rate of 10°C/min up to 1150°C. The tests were performed under a synthetic air flow of 80 mL/min. For each test, ~ 25 mg of material was weighed and stored in the same temperature and relative humidity controlled conditions before analysis.

Scanning electron micrographs of the fibers were performed to detect potential surface defects induced by aging. The pictures were taken with a Philips XL30 Scanning Electron Microscope in the Secondary Electron (SE) mode, to observe the surface topography, at 12 kV voltage and a working distance of 10 mm.

Tensile tests were performed on single fibers using a Zwick 1474 tensile testing machine with a 5N load cell and a rate of extension of $\sim 10\%$/min at 20°C. Similar conditions have been chosen in previous studies.[14,15] The fiber diameter was measured before each test using a laser micrometer Mitutoyo LSM-500S mounted on the tensile testing machine. The precision of the laser micrometer is ± 0.1 μm. Around 15 valid measurements were considered for each condition and duration of aging. A measurement is considered as valid whenever the tensile fracture does not occur near the clamps. The tensile
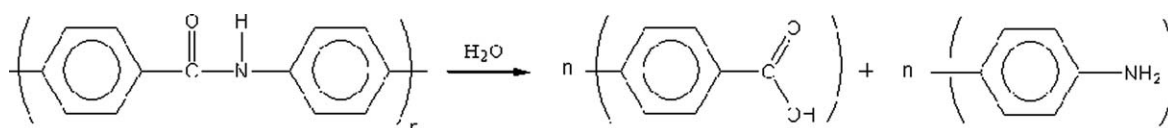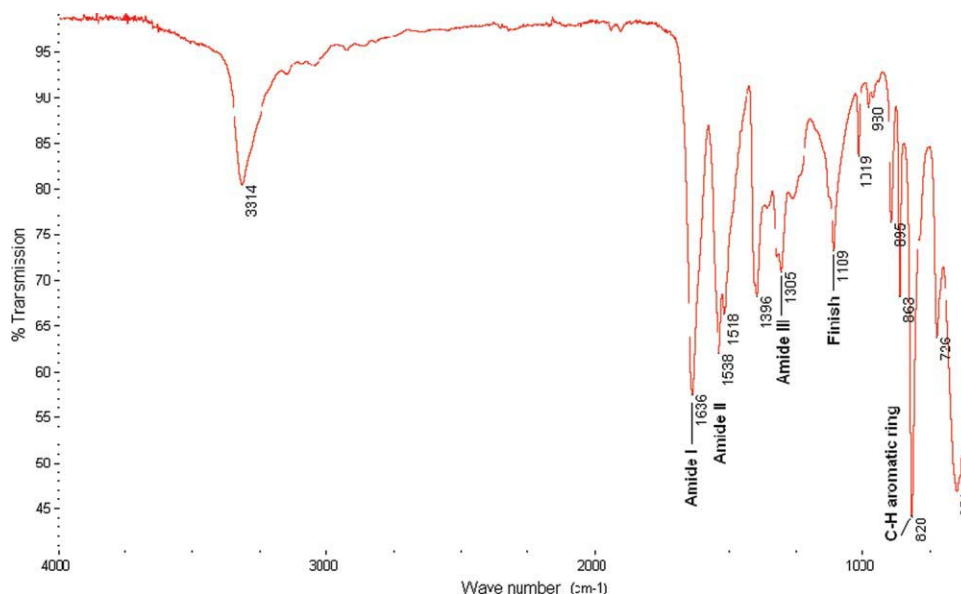

Figure 2 Hydrolysis of PPTA.

Figure 3 FTIR spectrum of as-received Twaron 1000 fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

modulus was calculated between 0.3 and 0.6% elongation.

RESULTS AND DISCUSSION

Influence of the finish on the surface degradation

Twaron fibers

The evolution of the normalized intensity of the peaks related to the finish and amide functions have been followed by FTIR to evaluate the surface hydrolysis of Twaron fibers with different initial finish contents. An infrared spectrum of Twaron 1000 as-received fibers is shown in Figure 3.

To perform semiquantitative analysis, the peaks were normalized using the peak located at ~ 820 cm^{-1} assigned to the C—H deformation of aromatic rings, for which the intensity appears to be constant throughout the aging duration. The intensity of the peak

located at 1109 cm^{-1} has been shown to depend on the finish content: it is significantly larger for Twaron 1000 fibers (0.6–1 wt % of finish) than for Twaron 1010 fibers (0.14 wt % of finish). This peak has thus been attributed to the finish. The amide function peaks have been identified as follows: the first peak located at ~ 1636 cm^{-1} is related to the C=O vibration (amide I), the second at ~ 1538 cm^{-1} is related to the combined motion of N—H bending and C—N (amide II), and the last at 1305 cm^{-1} is related to the C—N, N—H, and C—C combined vibrations (amide III).[16–18]

Table I groups the normalized intensity of the peaks related to the finish and to the amide functions (amide I at 1636 cm$^{-1)}$ for Twaron 1000 and Twaron 1010 fibers after 1 year aging at pH 11 and pH 9. The normalized intensity of a peak is a ratio, expressed in %, between the intensity of this peak and the intensity of an invariant peak (in our case the peak located at ~ 820 cm^{-1}).

TABLE I
Normalized Intensity of the Peaks Related to the Amide I and Finish of Twaron Fibers As-Received and After 1 Year

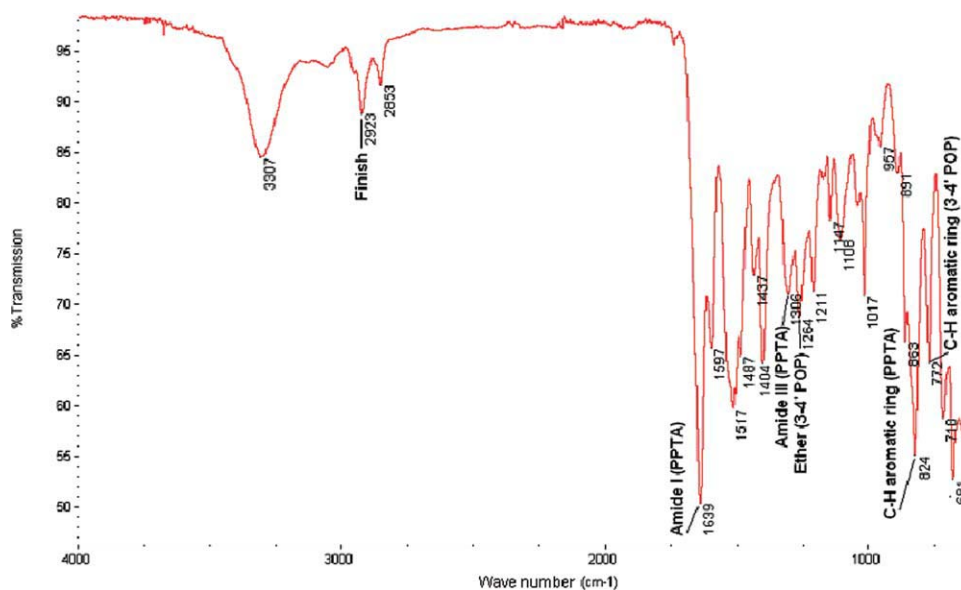| | Twaron 1010 (0.14 wt % of finish) | | Twaron 1000 (0.6–1 wt % of finish) | |
	Amide I	Finish	Amide I	Finish
As-received	100 ± 0.5	100 ± 2.8	100 ± 1.7	100 ± 4.5
pH 11				
80°C	98.6 ± 1.7	91.8 ± 1.3	96.2 ± 0.9	85 ± 0.1
20°C	98.4 ± 2.6	94.9 ± 1.1	96.7 ± 1.6	87.7 ± 0.8
pH 9				
80°C	96.8 ± 1.7	87.8 ± 1.5	96.1 ± 0.4	81.4 ± 0.3
20°C	98.5 ± 1.2	91.7 ± 2.5	97.1 ± 3.2	81.1 ± 2.6

Figure 4 FTIR spectrum of as-received Technora T240 fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

It appears that the finish removal does not depend strongly on the temperature. However, the pH seems to affect it to a greater extent: the more the solution is basic, the lower the finish loss. This result indicates that the presence of Na_2CO_3 in the solution may form a "protective layer" at the surface of the fibers that would limit the finish removal. As for the chains degradation, the decrease in the peak related to amide functions appears to depend neither on the temperature nor on the pH. The hydrolysis rates noted here are relatively low (between 1 and 4% decrease) and similar for Twaron 1000 and Twaron 1010 fibers. Thus, the finish content does not have any influence on the surface hydrolysis of Twaron fibers.

Technora fibers

In a similar way, the evolution of the normalized intensity of the peaks related to the finish and amide functions have been followed to evaluate the surface hydrolysis of Technora fibers with or without initial finish contents. An infrared spectrum of Technora T240 as-received fibers is shown in Figure 4.

The peaks were normalized using the peak located at $\sim$ 824 cm^{-1} attributed to the C—H deformation of PPTA sequence aromatic rings, for which the intensity and area appeared to be constant throughout the aging duration. By comparison between Technora T240 and Technora T000 spectra, the peak located at $\sim$ 2923 cm^{-1} has been attributed to the finish. This latter peak has been normalized using the peak areas, which appeared to be a more reliable method to evaluate the finish departure of Technora T240 fibers. As Technora fibers contain PPTA sequences, Technora

and Twaron fibers spectra have some peaks related to the amide functions in common: the peak located at $\sim$ 1639 cm^{-1} is related to the C=O vibration and the peak at $\sim$ 1306 cm^{-1} is related to the C—N, N—H, and C—C combined vibrations. The peaks related to the amide functions of PPTA and 3–4' POP sequences are not clearly dissociated. Technora displays extra peaks due to the 3–4' POP sequences: the peak located at $\sim$ 1264 cm^{-1} is related to the C—O vibration of the ether function, and the peak at $\sim$ 770 cm^{-1} is related to C—H deformation of meta-substituted aromatic rings.[19]

Table II groups the normalized intensity of the peaks related to the finish and to the amide functions (amide I) for Technora T240 and Technora T000 fibers after 1 year aging at pH 11 and pH 9.

These results indicate important finish removal for all the conditions. At pH 11, it appears that the finish removal is influenced by the temperature: the higher the temperature, the lower the finish loss. This may be explained by a crosslinking of the finish accelerated at the higher temperature. At pH 9, the temperature dependence of the finish loss is not obvious, within the accuracy of measurements. However, it may be concluded that the finish removal is of the same order at pH 9. As for the chains degradation, the decrease in the peak related to amide functions depends on the temperature and on the pH: this decrease is especially marked at pH 11 and 80°C for Technora T000 fibers. At pH 11 and 80°C, the presence of finish would thus limit the degradation of amide functions by forming a "protective layer" toward surface hydrolysis. For the other conditions, the presence of finish has little influence on the surface degradation.

TABLE II
Normalized Intensity/Area of the Peaks Related to the
Amide I and Finish of Technora T000 and Technora T240
Fibers As-Received and After 1 Year

	Technora T000 (0 wt % of finish)	Technora T240 (2.5 wt % of finish)	
	Amide I (%)	Amide I (%)	Finish (%)
As-received	100 ± 1.1	100 ± 0.4	100 ± 32.7
pH 11			
80°C	87.8 ± 0.4	97.2 ± 1.6	17.6 ± 4.9
20°C	97.8 ± 1.3	98.9 ± 1.2	6.7 ± 1.2
pH 9			
80°C	94.6 ± 0.9	95.5 ± 0.2	16.1 ± 2.3
20°C	97.3 ± 2.3	99.1 ± 0.6	12.7 ± 5.9

Influence of the finish on the bulk degradation

After evaluating the influence of the finish on the surface hydrolysis of Twaron and Technora fibers, its influence on the bulk degradation has been studied by viscosimetry.

Twaron fibers

By comparing Twaron 1000 and Twaron 1010 as-received fibers, it appears that the finish content does not have any significant influence on the reduced viscosity. Indeed, the reduced viscosity is 1105 mL/g for Twaron 1000 fibers and 1150 mL/g for Twaron 1010 fibers. The weight average molecular mass is not significantly affected by the finish content: M_w is 32,100 g/mol for Twaron 1000 fibers, 32,200 g/mol for Twaron 1010 fibers. Although, as the reduced viscosity at 2×10^{-3} g/mL does not involve any extrapolation to be calculated, it is a

more precise indicator to highlight low degradation rate. It will be chosen in the following discussion.

Figure 5 displays the reduced viscosity at 2×10^{-3} g/mL of Twaron 1000 and Twaron 1010 fibers aged at pH 11 and pH 9. From a series of three experiments, the precision of the reduced viscosity at 2×10^{-3} g/mL has been estimated at ±20 mL/g for the Twaron 1000 as-received fibers, and at ±15 mL/g for the Twaron 1010 as-received fibers.

At pH 11, the reduced viscosity of Twaron 1000 and Twaron 1010 fibers display the same logarithmic evolution [Fig. 5(a)]. At pH 9, the reduced viscosity also follows a logarithmic evolution with time, and the degradation appears to be slightly larger for Twaron 1010 fibers [Fig. 5(b)].

The logarithmic evolutions observed here have been previously interpreted as the result of two degradation processes at pH 11, namely the destruction of the tie-molecules/fibrils and the degradation of the crystallites, and one degradation process at pH 9, namely the destruction of the tie-molecules/fibrils only.[20] The results reveal that the finish content may not change the degradation mechanisms: the degradation curves of Twaron 1010 fibers seem to conserve a logarithmic relation with time. Moreover, it appears that higher the initial finish content, lower the degradation rate. The finish may thus act as a "protective layer" that limits the diffusion of the solution into the fiber, lowering the bulk degradation.

Technora fibers

As for Twaron fibers, viscosity measurements of Technora fibers aim at highlighting chain scissions occurring during aging. Table III groups the reduced viscosity of Technora fibers with or in the absence of finish treatment. From a series of three experiments,
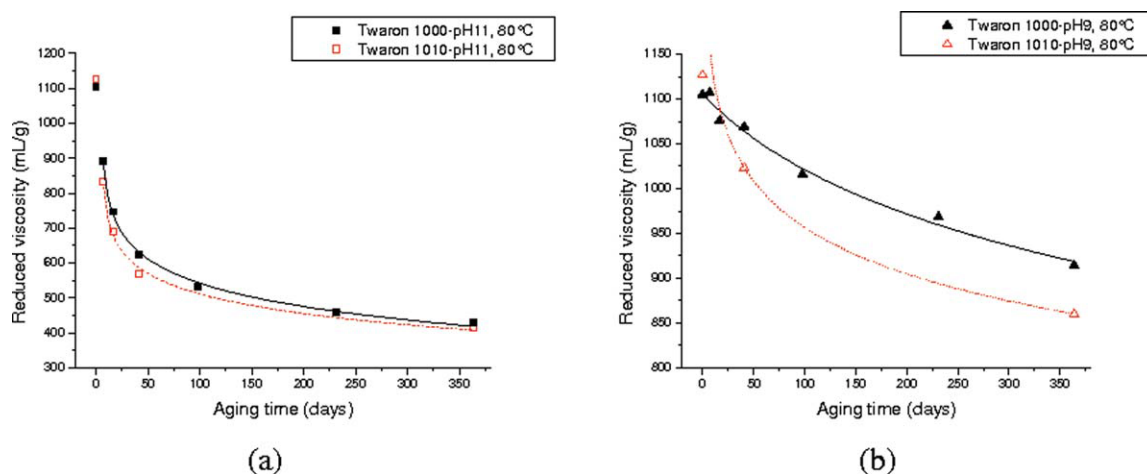

(a)   (b)

Figure 5 Evolution of the reduced viscosity at 2×10^{-3} g/mL for Twaron fibers aged (a) at pH 11 and (b) at pH 9. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Reduced Viscosity of Technora T000 and Technora T240 Fibers, As-Received and After 1 Year Aging, Expressed in mL/g

	Technora T000 (0 wt % of finish)	Technora T240 (2.5 wt % of finish)
As-received	498	441
pH 11, 80°C	469	497
pH 9, 80°C	466	450

the precision of the reduced viscosity has been estimated at ±60 mL/g for the Technora T240 as-received fibers and at ±30 mL/g for the Technora T000 as-received fibers.

By comparing Technora T240 and Technora T000 as-received fibers, it appears that the presence of finish lowers the reduced viscosity significantly. The finish used for these fibers may thus be a low molecular mass compound that reduces the global reduced viscosity.

For Technora T000 fibers, the reduced viscosity decreases: chain scission does, therefore, occur under these conditions. The decrease is similar at pH 9 and pH 11, indicating that the pH has no significant influence on the bulk degradation.

For Technora T240 fibers, the reduced viscosity evolution may result from a combination between finish removal, leading to an increase in the reduced viscosity, and chain scissions, leading to a decrease in the reduced viscosity. The global increase in the reduced viscosity observed both at pH 9 and pH 11 must result from predominant finish departure. These results do not allow chain scissions phenomena to be highlighted, but this does not mean that they do not occur. Thermogravimetry analyses have been performed to give complementary information.

Influence on the thermal characteristics

An example of a thermogravimetric curve (TG) together with the derived thermogravimetric curve (DTG) is given on Figure 6 for Twaron 1000 as-received fibers.

The first weight loss up to 175°C depends on the storage conditions. It is thus attributed to the sorbed water departure. From 175°C to the decomposition, the weight loss is assigned to the finish decomposition. Finally, the beginning of the most important weight loss at 498°C was identified as the onset decomposition temperature of the PPTA itself.

In a similar way, for as-received Technora T240 fibers, the sorbed water removal is located between ambient temperature and 140°C, the residual finish content between 140°C and the decomposition temperature.
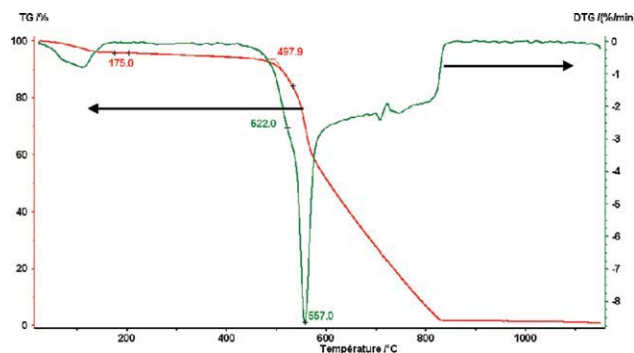

Figure 6 Thermogravimetric and derived thermogravimetric curves of Twaron 1000 fibers at 10°C/min under synthetic air atmosphere. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Twaron fibers

Table IV groups the decomposition temperature of Twaron fibers measured by TGA. From a series of five experiments, the precision of the decomposition temperature measurement has been estimated at ±4°C.

It appears that the decomposition temperature of Twaron 1000 and Twaron 1010 as-received fibers are close: the finish content has little influence on the decomposition temperature of as-received fibers. The decomposition temperature decreases after 1 year at pH 11 and 80°C for both kinds of Twaron, but slightly more for Twaron 1010 fibers. In a similar way, after 1 year at pH 9 and 80°C, the decomposition temperature decreases for Twaron 1010 fibers, whereas it remains unchanged for Twaron 1000 fibers. Therefore, it appears that higher the initial finish content, less the decomposition temperature of hydrolytically aged Twaron fibers decreases.

By analogy with viscosity measurements, it can be noted that the decomposition temperature globally decreases with reduced viscosity. Indeed, it is likely that low-molecular-weight chains decompose at lower temperature. From this assumption, it appears that the finish content of Twaron fibers has a slight influence on the hydrolytic degradation: lower the initial finish content, lower the decomposition temperature, and thus larger the chain degradation rate.

TABLE IV
Decomposition Temperatures of Twaron Fibers As Received and After 1 Year Aging

|	Twaron 1010 (0.14 wt % of finish)	Twaron 1000 (0.6–1 wt % of finish)
As-received	495°C	498°C
pH 11, 80°C	473°C	479°C
pH 9, 80°C	489°C	496°C

TABLE V
Decomposition Temperatures of Technora Fibers
As-Received and After 1 Year Aging

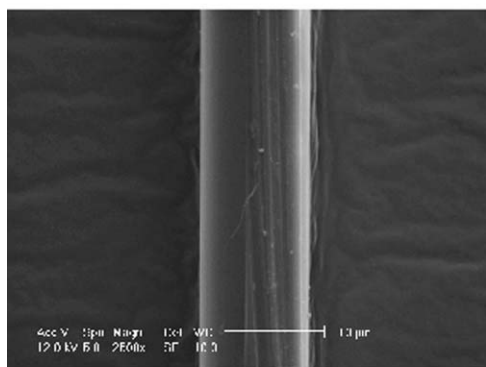|	Technora T000 (0 wt % of finish)	Technora T240 (2.5 wt % of finish)
As-received	474°C	472°C
pH 11, 80°C	452°C	463°C
pH 9, 80°C	457°C	462°C

As mentioned in the previous section, the finish may thus act as a protective layer which limits hydrolytic degradation. Thermogravimetric analysis could thus
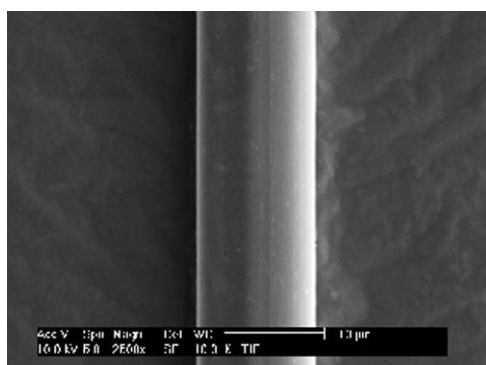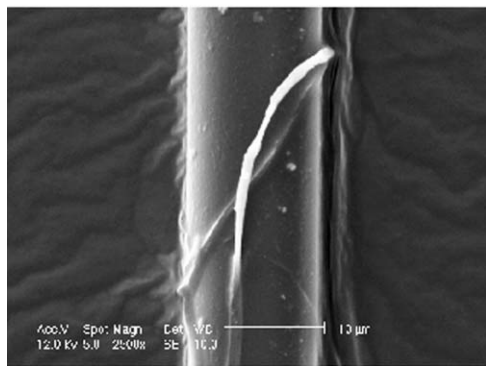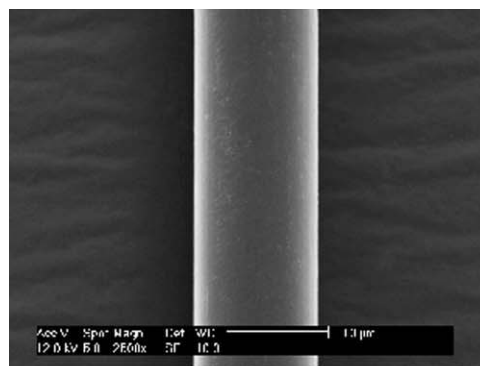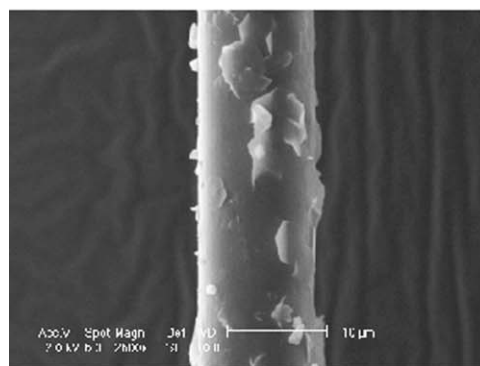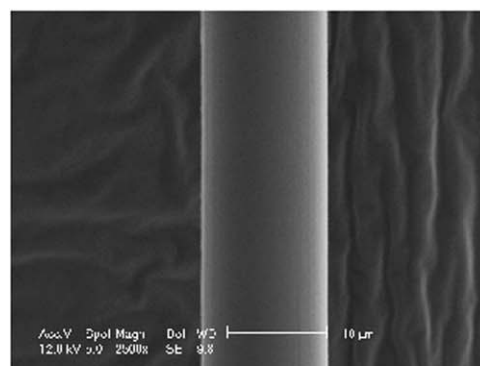

Figure 7 SEM observations in SE mode of Twaron 1010 fibers (a) as-received, (b) after 1 year at pH 11 and 80°C, and (c) after 1 year at pH 9 and 80°C.
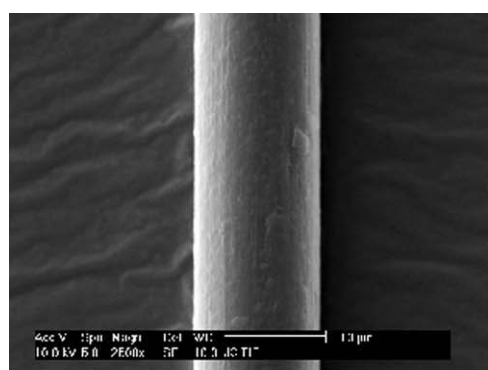
Figure 8 SEM observations in SE mode of Twaron 1000 fibers (a) as-received, (b) after 1 year at pH 11 and 80°C, and (c) after 1 year at pH 9 and 80°C.

prove to be a complementary technique to viscosity measurements to reveal chain degradations.

Technora fibers

Table V groups the decomposition temperatures of Technora fibers measured by TGA. From a series of tests on six samples, the precision of the decomposition temperature measurement has been estimated at ±4°C.
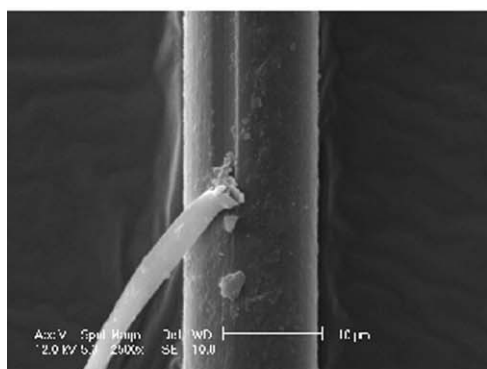
It appears that the decomposition temperature of Technora T240 and Technora T000 as-received fibers are similar: the presence of finish has little influence on the decomposition temperature. After 1 year at
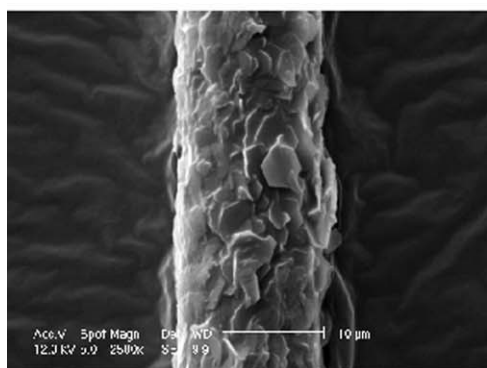
Figure 9   SEM observations in SE mode of Technora T000 fibers (a) as-received, (b) after 1 year at pH 11 and 80°C, and (c) after 1 year at pH 9 and 80°C.

pH 11 and at pH 9 at 80°C, this temperature decreases for both kind of Technora fibers. The decrease is slightly larger for Technora T000 fibers for all the conditions. The presence of finish limits the decomposition temperature decrease.

By analogy with viscosity measurements, it can be noted that the decomposition temperature of Technora T000 fibers decreases with the reduced viscosity. As for Twaron fibers, it would be likely that low-molecular-weight chains decompose at lower temperature. As the decomposition temperature is lower for Technora T000 for all the aging conditions, it can be concluded that the degradation of Technora fibers is

larger without finish treatment. The finish may thus act as a protective layer which limits hydrolytic degradation. As TGA permit to reveal chain degradations for Technora fibers, it could be considered as a complementary technique to viscosimetry. The evolution of the reduced viscosity observed previously for Technora T240 fibers do thus come from a combination between chain degradations and finish removal.
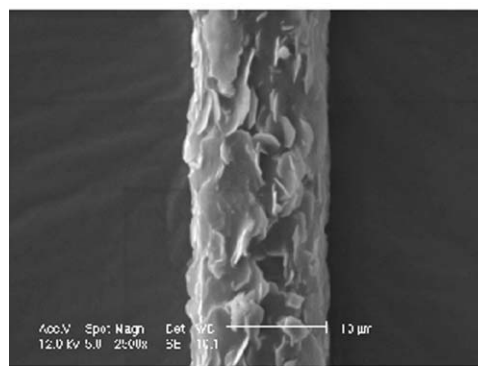
Influence of the finish on the surface state

Twaron fibers
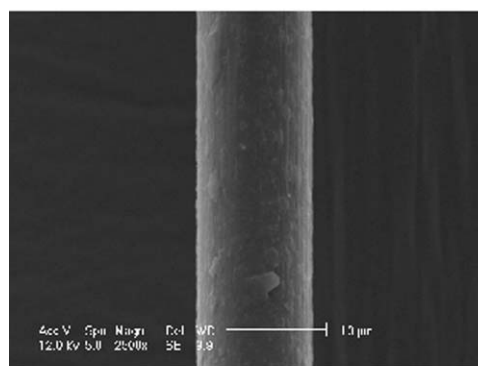
Figures 7 and 8 group the SEM observations of Twaron fibers aged under different basic conditions.
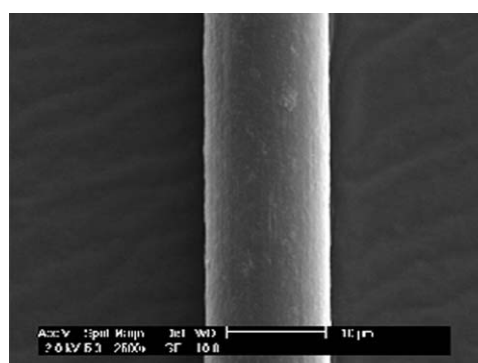
Figure 10   SEM observations in SE mode of Technora T240 fibers (a) as-received, (b) after 1 year at pH 11 and 80°C, and (c) after 1 year at pH 9 and 80°C.
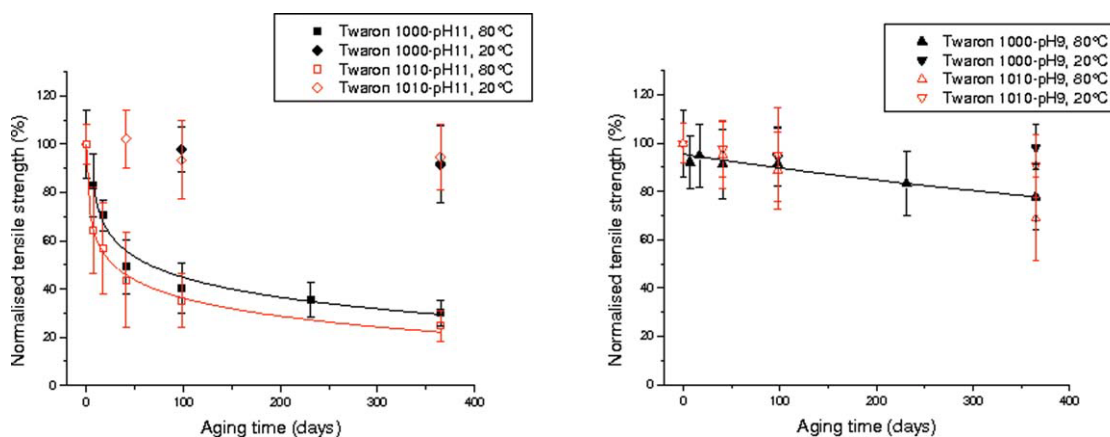
Figure 11 Evolution of the tensile strength of Twaron fibers aged at pH 11 and pH 9. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

It should be noted that there is no significant evolution of the diameter of Twaron fibers over the aging period considered here: whatever the aging condition, it remains between ~ 11.5 and 12.2 μm.

The surfaces of Twaron 1000 and Twaron 1010 as-received fibers do not display any defects. After 1 year at pH 9 and pH 11, the fibers with lower finish content globally display more fibril departure resulting in more longitudinal grooves at the surface. These defects may be attributed to abrasion probably due to the stirring of the solutions. It appears thus that the resistance to abrasion is improved with higher finish content. After 1 year at pH 11 and 80°C, Twaron 1000 fibers present some excoriated layers (some of these seem to be hexagonal), which may be due to rearrangement of some drawing agent embedded in the surface.

Technora fibers

Figures 9 and 10 group the SEM observations of Technora fibers.

The fibers diameter has been measured using the laser micrometer and by SEM. There is again no significant evolution of the diameter of Technora fibers over the aging period considered here: whatever the aging condition, it remains between ~ 11.5 and 12.4 μm. The surfaces of Technora T240 and Technora T000 as-received fibers do not display any defects. After 1 year at pH 9 and 80°C, the fiber without finish globally displays more fibril removal than Technora T240, resulting in more longitudinal grooves at the surface. As for Twaron fibers, these defects may be attributed to abrasion probably due to the stirring of the solutions. It appears thus that the resistance to abrasion is improved with higher finish content. After 1 year at pH 11 and 80°C, Technora T000 and Technora T240 fibers both display some excoriated layers, which may again be due to rearrangement of drawing agent on the surface.

Influence on the mechanical properties

After evaluating the changes in chemical, thermal, and morphological characteristics of hydrolytically aged aramid fibers, it is interesting to investigate how they affect the functional properties. Tensile tests were, therefore, carried out to identify the changes responsible for mechanical property evolutions. The tensile properties (tensile strength and tensile modulus) have been expressed in Newtons and then normalized with respect to the as-received values, to avoid any error due to the slight differences measured in diameters. Therefore, the slope of the force-strain curves does not provide the tensile modulus but is indicative of the residual stiffness of the fibers.

Twaron fibers

Figure 11 groups the tensile strength changes of Twaron 1000 and Twaron 1010 fibers aged at pH 11 and pH 9.

It appears that the tensile strength drop is larger at pH 11 than at pH 9 and larger at 80°C than at 20°C. At pH 11 and 20°C, there is no influence of the finish content on the tensile strength degradation rate. In the other conditions, there is only a slight

TABLE VI
Residual Stiffness of Twaron 1010 and Twaron 1000 After 1 Year Aging at pH 11 and pH 9

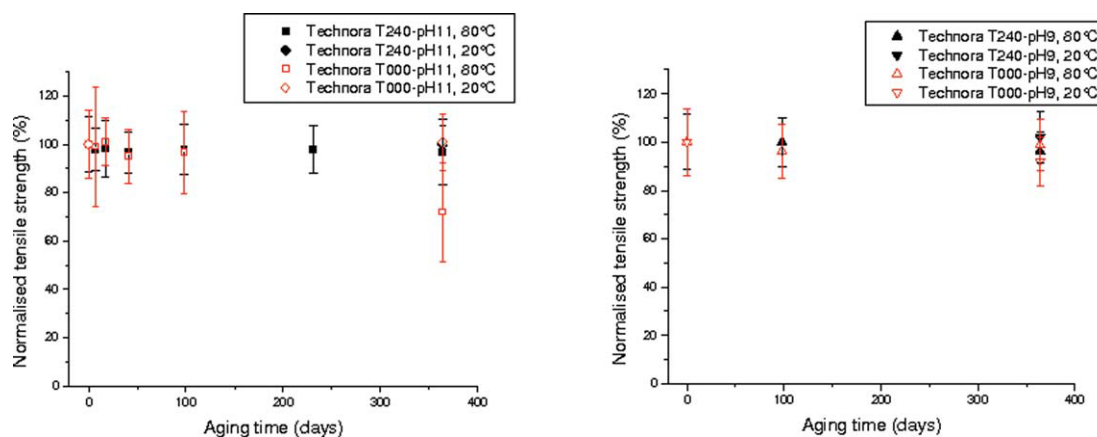|	Twaron 1010 (0.14 wt % of finish)	Twaron 1000 (0.6–1 wt % of finish)
As-received	100% ± 7%	100% ± 13%
pH 11		
80°C	92% ± 14%	96% ± 10%
20°C	94% ± 13%	97% ± 13%
pH 9		
80°C	96% ± 8%	97% ± 11%
20°C	99% ± 7%	97% ± 11%

Figure 12 Evolution of the tensile strength of Technora fibers aged at pH 11 and pH 9. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

influence of the finish content on the tensile strength evolution: the strength degradation is slightly higher with a lower initial finish content.

At pH 11 and 80°C, it appears that the degradation is accelerated at the beginning of aging in the absence of finish, but the degradation rates reach a similar value at longer aging times. Consequently, the higher the finish content, the more the fibers are "protected" toward tensile strength degradations. This may be attributed to the lower bulk degradation and less surface damage observed for the fibers with higher finish content.

Table VI presents the residual tensile modulus of Twaron fibers after one year aging at pH 11 and pH 9.

The tensile modulus does not vary significantly over the aging time considered here. Whatever the aging conditions, the finish content does not have any significant influence on the tensile modulus: its value levels off throughout aging. As explained previously,[20] the structural changes induced by aging at pH 9 and pH 11 affect the tensile strength but not the tensile modulus.

Technora fibers

Figure 12 groups the tensile strength evolutions of Technora T240 and Technora T000 fibers aged at pH 11 and pH 9.

The decrease in the tensile strength is not significant under any conditions, except at pH 11 and 80°C for the Technora T000 fibers where the decrease reaches almost 30%. Consequently, the presence of finish protects the fibers toward tensile strength degradations occurring at pH 11 and 80°C. At pH 9, the tensile strength is not affected by the presence of finish, even though slightly higher bulk degradation and more surface damage have been observed for the Technora T000. At pH 11 and 80°C, the higher surface degradation rate of Technora T000 fibers may explain the larger tensile strength decrease. The

surface degradation of Technora fibers would thus govern the tensile strength conservation.

The high stability of Technora fibers in water and in moderately alkaline conditions has been reported elsewhere.[21] Imuro and Yoshida[6] postulated that the superior chemical-resistance of Technora arises from the total effect of (a) the dilution of aramid linkages by less chemically reactive ether-linkages, (b) the high orientation of the amorphous part, which prevents water and chemical agent from penetrating into the fiber, and (c) its dense structure.

Table VII presents the residual tensile modulus of Technora fibers after one year aging at pH 11 and pH 9.

Once again, the tensile modulus does not vary significantly over the aging time considered here.[21]

CONCLUSIONS

The influence of the finish on the durability of Twaron and Technora fibers under an alkaline environment has been evaluated by FTIR, viscosity measurements, TGA, and tensile tests. Several conclusions may be proposed as follows:

- Finish departure has been revealed under exposure to basic conditions.

TABLE VII
Residual Stiffness of Technora T000 and Technora T240 After 1 Year Aging at pH 11 and pH 9

	Technora T000 (0 wt % of finish)	Technora T240 (2.5 wt % of finish)
As-received	100% ± 9%	100% ± 8%
pH 11		
80°C	100% ± 8%	102% ± 7%
20°C	99% ± 6%	98% ± 7%
pH 9		
80°C	100% ± 8%	97% ± 5%
20°C	92% ± 10%	103% ± 9%

- For Twaron fibers, higher finish content appears to reduce the tensile strength degradation. The finish may act as a barrier that slightly limits bulk hydrolytic degradation and improves the resistance to abrasion. For all the conditions, the finish content does not affect the modulus.
- For Technora fibers, the presence of finish appears to reduce the tensile strength degradation at pH 11 and 80°C only. For these conditions, the finish may act as a barrier that limits bulk and surface hydrolytic degradation and improves the resistance to abrasion. Even though the bulk degradation and abrasion are also limited at pH 9 and 80°C with higher finish content, the tensile strength conservation is not improved. The surface degradation is thus a serious concern for tensile strength conservation in an alkaline environment. For all the conditions, the finish content does not affect the tensile modulus.
- The finish content is shown to have some influence on the aramid fibers durability. The lifetime of aramid geotextiles may be improved by application of a nonsoluble finish treatment.

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