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Degradation of *Technora* aramid fibres in alkaline and neutral environments

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Abstract:

Technora fibres are high performance aramid fibres which have been used in ropes and protective clothing for many years. They are also now being proposed as geotextiles for soil reinforcement. However, there is a lack of experience on the long-term behaviour of *Technora* fibres in an alkaline environment (lime-treated ground…). Consequently, aging studies have been performed under different conditions (deionised water, pH9 and pH11). Hydrolytic degradation has been evaluated by FTIR, viscometry, TGA, density measurements, SEM, and by tensile measurements. Some chain degradation and finish rearrangements have been highlighted, but *Technora* fibres retain their mechanical properties for all the conditions considered here.

Keywords: Aramids; Fibres; Technora; Hydrolysis; Long-term behaviour

1. Introduction

Because of the premature aging of polyethylene terephtalate fibres in alkaline ground (lime, cement or slag treated soils, next to the skin of hardened concrete, etc…) [1], other materials are being considered for ground reinforcement. These include *Technora* aramid fibres [2, 3], which are well-known for their use in ropes and cables, in textiles for heat and cut protection and in composites. *Technora* fibres are based on copoly-(paraphenylene/3,4'-oxydiphenylene terephtalamide) (Figure 1) [4].

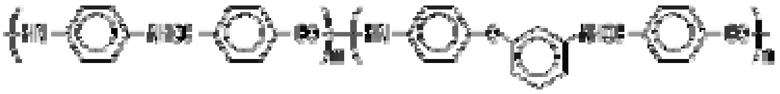


Figure 1: co-poly-(paraphenylene/3,4'-oxydiphenylene terephthalamide) (Technora®) molecular structure

Imuro and Yoshida [5] proposed a structural model for *Technora* fibres (HM-50 grade) consisting of both random sequences in an alternating distribution and block copolymer parts. The well-oriented and fully-extended macromolecular chains are composed of 70-90 Å long flexible segments (made of 3-4' POP sequences) and 110-130 Å long rigid segments (made of PPTA sequences). They do not display any skin-core structure.

Technora fibres contain amide functions that are sensitive to hydrolysis [6], although the dilution of aramid-linkages by less chemically reactive ether-linkages contributes to better chemical resistance than pure aramids [5]. The hydrolytic degradation mechanism involves scission of the amide N-H linkage, yielding acid and amine functions (Figure 2) [5-7].

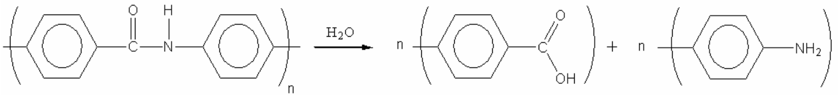


Figure 2: Hydrolysis of amide functions

Imuro and Yoshida [5] reported that the tensile strength of *Technora* (HM-50) fibres does not decrease after 400 hours exposure in 120°C saturated steam, whereas it decreases by 80% for PPTA fibres. In a similar way, the tensile strength of *Technora* fibres was shown to decrease by 25% after 100 hours exposure in a 10 wt% NaOH solution at 95°C, whereas it decreases by 80% for PPTA fibres. The short term hydrolysis resistance of *Technora* fibres appears to be considerably better than that of standard aramids, but their long-term behaviour in water and in moderately alkaline solutions has not been studied yet. This work studies the degradation mechanism of *Technora* fibres under these conditions by identifying the changes in chemical, structural and morphological characteristics and their influence on the mechanical properties.

2. Experimental

2.1 Materials

The *Technora T240* fibre studied in this paper, in the form of 1670 dtex yarn, is a para-aramid fibre produced by TeijinAramid.

2.2 Aging methods

Three aging environments have been chosen. Yarn samples were immersed in buffer sodium carbonate salt solutions at pH9 and pH11, and in deionised water. Deionised water was produced by a Rios water purification system, circulating and continuously renewed. Four temperatures have been considered for each aging condition: 20, 40, 60 and 80°C. Over the aging period considered here the temperature variability is estimated at +/-2°C.

2.3 Analysis and characterization

Fourier Transformed Infrared spectrometry
FTIR spectroscopy analysis of the fibres was performed in Attenuated Total Reflectance (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 analysed with *OMNIC 3.1* software. Each scan was made with a yarn, composed of 1000 filaments, and repeated three times per sample and aging condition.

Viscosity measurements
Viscosity measurements were carried out using an Ubbelohde DIN (*Schott Instruments*) capillary viscosimeter, at 25°C. The reduced viscosity measurements were performed at three concentrations between 3.10^{-4} g/mL and $1.5.10^{-3}$ g/mL. The fibres were dissolved in 50 mL of sulphuric acid concentrated at 96% for two hours at 60°C with magnetic stirring. Because of the presence of ether linkages, *Technora* fibres are more susceptible to strong acid exposure than pure aramid *Twaron* fibres [8]. The remaining insoluble fractions after dissolution were extracted and weighed to calculate the true concentration of the solution.

Thermogravimetric analysis
Thermogravimetry continuously measures the mass of a sample subjected to a steady increase of temperature. The thermal analyser 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.

Density measurements
The samples were successively weighed at 20 ± 1°C in ambient air and immersed in dodecane, which appears to be inert and not absorbed by the *Technora* fibres. Then, the density of the fibres, ρ_{fibres}, was calculated using the following relation:

$$\rho_{fibres} = \frac{m_1 \times \rho_{dodecane} - m_2 \times \rho_{air}}{m_1 - m_2} \qquad (1)$$

where m_1 is the mass weighed in air, m_2 is the mass weighed in dodecane, ρ_{air} is the density of air, and $\rho_{dodecane}$ is the density of dodecane.

The corresponding porosity rate, $V_{porosity}$, was calculated using the following relation:

$$V_{porosity} = 1 - \rho_{fibres}\left(\frac{M_{finish}}{\rho_{finish}} + \frac{M_{PPTA}}{\rho_{PPTA}}\right) \qquad (2)$$

where M_{finish} and M_{PPTA} are respectively the finish and the polymer (that is to say without any finish) weight percentages, ρ_{finish} and ρ_{PPTA} are respectively the finish and the polymer densities.

The fibres were dried beforehand for 48 hours in a vacuum oven at 90°C [9] to remove the water absorbed by the fibres, and then stored at 30°C with silicagel.

Scanning Electron Microscopy

Scanning electron micrographs of the fibres were taken to detect surface defects induced by aging. A Philips XL30 Scanning Electron Microscope was used in the Secondary Electron (SE) mode, in order to observe the surface topography, at 12 kV voltage and a working distance of 10 mm.

Tensile tests

Tensile tests were performed on single fibres using a *Zwick 1474* tensile testing machine with a 5N force sensor and a rate of extension of 10%/min, at 20°C. The fibre diameter, ~11.5 µm on average, 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 fifteen valid measurements were considered for each condition and duration of aging. The tensile modulus was calculated between 0.3 and 0.6% elongation.

3. Results and discussion

Several characteristics have been followed during the aging: the surface and bulk chemical degradation, physical evolutions and the surface state of the fibres. Then, the influence of these characteristics on the mechanical properties has been evaluated.

3.1 Evaluation of the surface degradation: FTIR-ATR

An FTIR-ATR spectrum of *Technora T240* as-received fibres is given in Figure 3. After extraction of the finish with deionised water at ambient temperature, FTIR analyses of the isolated finish enable the peak located at ~2923 cm^{-1} to be attributed to the finish. As *Technora* fibres contain PPTA sequences similar to *Twaron* fibres, the spectra display some peaks related to the amide functions in common [10]: the peak located at ~1639 cm^{-1} is related to the C=O vibration and the peak at ~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 ~1264 cm^{-1} is related to the C-O vibration of the ether function, and the peak at ~770 cm^{-1} is related to C-H deformation of meta-substituted aromatic rings [4]. In order to perform semi-quantitative analyses, the peaks were normalised using the peak located at ~824 cm^{-1} attributed to the C-H deformation of the PPTA sequence aromatic rings which remains constant throughout the aging duration.

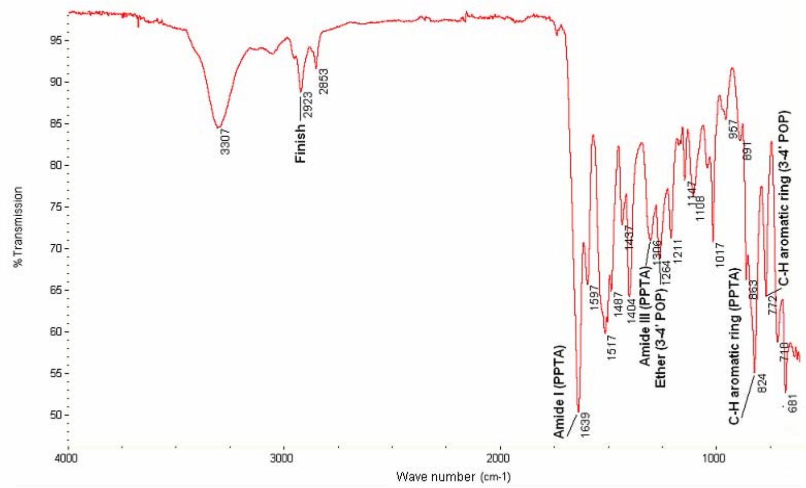


Figure 3: FTIR-ATR spectrum of as-received Technora T240 fibres

Table 1 groups the evolutions of the peaks related to the amide I functions of *Technora T240* fibres aged in alkaline and neutral environments.

Table 1: Normalised intensity of the peaks related to the amide I functions of Technora T240 fibres as received and after one year

		Amide I (%)
As-received		100 ± 0.4
pH11	80°C	97.2 ± 1.6
	20°C	98.9 ± 1.2
pH9	80°C	95.5 ± 0.2
	20°C	99.1 ± 0.6
Deionised water	80°C	97.1 ± 1.7
	20°C	100.8 ± 1.0

The small decrease in the amide I peak varies between 0 and 5% for all the conditions. This decrease highlights that some chain degradation occur at the surface of the fibres. The pH does not have any significant influence on the surface degradation. It must be noted therefore that the higher the temperature, the larger the degradation.

3.2 Evaluation of the bulk degradation

3.2.1 Viscosimetry

The reduced viscosity of *Technora T240* increases slightly from ~441 ± 60 mL/g to ~497 mL/g after one year at pH11 and 80°C, to ~450 mL/g after one year at pH9 and 80°C, and to ~492 mL/g after one year in deionised water at 80°C. The influence of the finish on the reduced viscosity have been explained elsewhere [11]. It appeared that the presence of finish lowers the reduced viscosity significantly. As the reduced viscosity evolution of aged *Technora T240* fibres may result from a combination between finish removal and potential chain scissions, it is impossible to evaluate the *Technora T240* bulk degradation reliably. Thermogravimetry analyses have been performed to give complementary information.

3.2.2 Thermogravimetry analysis

An example of a thermogravimetric curve together with the derived thermogravimetric curve is given on Figure 4 for *Technora T240* as-received fibres.

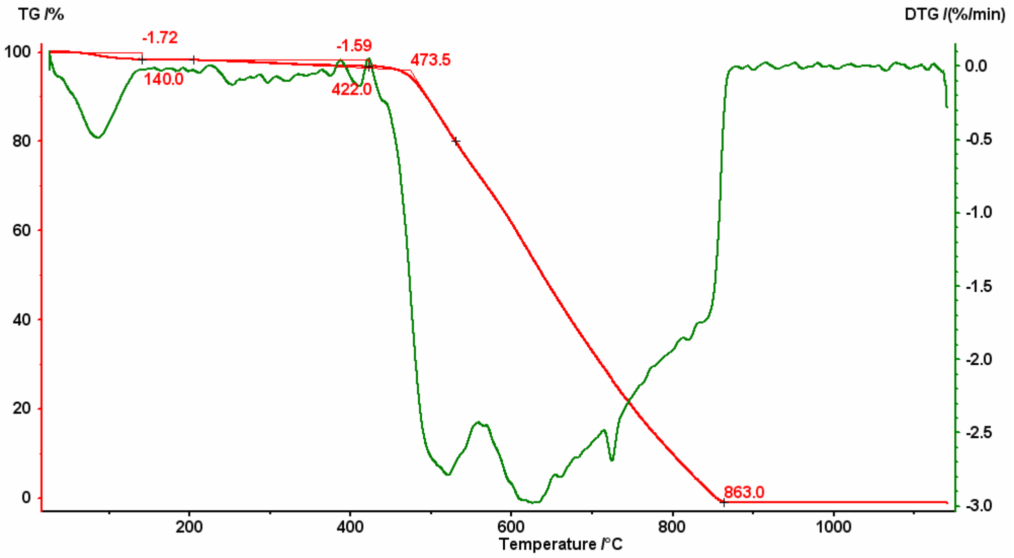


Figure 4: Thermogravimetric and derived thermogravimetric curves of Technora fibres heated up to 1100°C at 10°C/min under synthetic air atmosphere

The first weight loss up to 140°C, which was found to depend on the storage conditions, is attributed to the sorbed water departure. From ~140°C to the ~422°C, the weight loss is assigned to the finish decomposition. Finally, the beginning of the most important weight loss at 474 ± 4°C was identified as the onset decomposition temperature of the polymer. The polymer decomposition from 474 ± 4°C to ~863°C consists of two slopes which may be attributed to the decomposition of the PPTA and the 3,4' POP sequences, as reported by Ozawa [8]. This assumption is supported by the thermogravimetric curve of PPTA fibres which display only one slope for the main decomposition [11].

Table 2 groups the decomposition temperatures of *Technora T240* fibres as-received and after one year aging in different conditions.

Table 2: Decomposition temperatures of Technora T240 fibres measured by TGA

	Decomposition temperature (°C)
As-received	474
pH11, 80°C, 549 days	463
pH9, 80°C, 549 days	462
Deionised water, 80°C , 549 days	476

The decomposition temperature decreases by ~10°C after one year at pH11 and pH9 at 80°C, and does not decrease in deionised water at 80°C. The hypothesis which suggests that the lower the decomposition temperature the larger the chain degradation has been shown to be acceptable [11]. Indeed, it is likely that lower molecular weight chains are degraded at lower temperature. Moreover, the presence of finish does not have any influence on the decomposition temperature [11]. The present results suggest that hydrolytic aging of *Technora T240* fibres involves some chains degradation at pH9 and pH11, which could not be highlighted by viscosity measurements. Although no evidence of chain degradation in deionised water can be detected from these results.

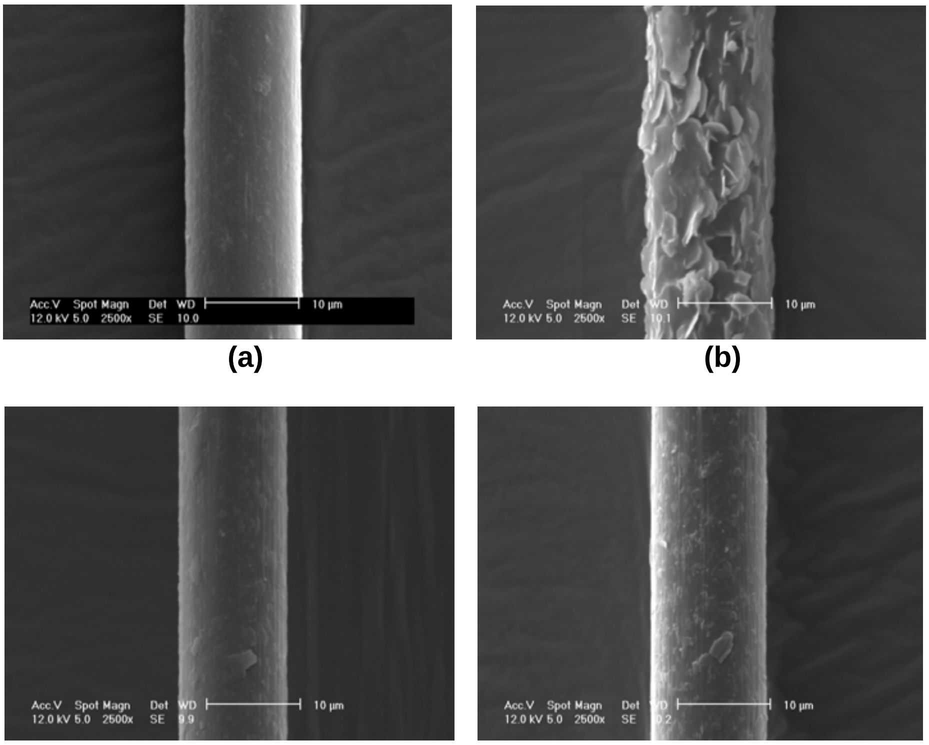
3.3 Physical evolutions: density measurements

The presence of finish has been shown to have a significant influence on the density of the *Technora* fibres [11]. For instance, the density is 1.398 ± 0.002 for as-received fibres without finish (*Technora T000*) whereas it is 1.387 ± 0.003 for as-received fibres with 2.5 wt% finish content (*Technora T240*). These values are in accordance with the density of 1.39 reported by Teijin [12]. Consequently, an "apparent" density, related to the density of the polymer only (that is to say without any finish content), has been calculated from FTIR-ATR measurements by determining the finish loss throughout the aging duration. The calculation is detailed elsewhere [13].

It appears that the porosity rate evolution of *Technora T240* fibres aged under different conditions is negligible.

3.4 Surface state evolutions: SEM

Figure 5 groups SEM pictures of *Technora T240* fibres before and after one year aging at 80°C at pH11, at pH9 and in deionised water.



(a) **(b)**

(c) **(d)**

Figure 5: SEM pictures of Technora T240 fibres (a) as-received, and after one year (b) at pH11 and 80°C (c), at pH9 and 80°C, and (d) in deionised water at 80°C

After one year at pH9 and in deionised water at 80°C, the fibres do not display any important surface defects. Local finish rearrangement in the form of small aggregates has been therefore observed in these conditions. After one year at pH11 and 80°C, the fibres display local randomly oriented hexagonal shapes, which are attributed to finish rearrangement as well.

Multi-scales analyses revealed that hydrolytic aging involves some degradation for *Technora T240* fibres. At first, slight chain degradation at the surface has been highlighted by FTIR-ATR for all the conditions. Then, Thermogravimetry reveal that bulk chain degradation occurs at pH9 and pH11. Although, no evidence of density evolutions have been noticed for all the conditions. Finally, the surface state of hydrolytically-aged fibres display some finish rearrangements. At present, we can wonder how the mechanical properties are affected by these evolutions.

3.5 Mechanical properties evolutions

Figure 6 shows typical stress-strain and modulus-strain curves for as-received *Technora T240* fibres.

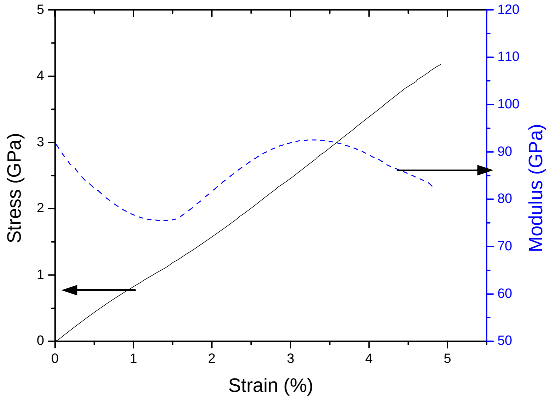


Figure 6: Stress-strain and modulus-strain curves for as-received Technora T240 fibres

The modulus curve first decreases with strain to a minimum at 1.2-1.5% strain, then increases to reach a maximum at 3-3.3% strain and finally decreases up to the tensile break. The modulus of aged fibres displays exactly the same trend and similar values for a given strain rate up to the tensile break. That is why the modulus can be compared in any strain range; in this study, we have chosen 0.3-0.6%.

Based on the work of Northolt and van der Hout [14], Yeh and Young [15] suggested that the increase in the modulus with strain results from crystallites orientation towards the fibre axis. Their modulus-strain curve display a similar behaviour with the exception that their modulus first increases up to 0.3% strain. It is thus likely that the different behaviour at low deformation observed here may be due to application of a preload force prior to their tensile tests; however it was not precised by the authors.

No significant evolution in diameter has been noticed for any condition or duration of aging: all the diameters are in the range from 11.3 to 11.9 µm. The initial tensile strength is 3.70 ± 0.42 GPa, and the modulus is 86 ± 7 GPa. However, to avoid any error due to the slight differences measured in diameters, the tensile properties will be expressed in Newton and then normalised.

Table 3 groups the mechanical properties after one and half years aging for all the conditions.

Table 3: Residual mechanical properties after one and half years aging

		Normalised tensile strength (%)	Normalised tensile modulus (%) at 0.3- 0.6% strain
As-received		100 ± 13	100 ± 8
pH11	80°C	96 ± 10	103 ± 8
	20°C	101 ± 13	99 ± 14
pH9	80°C	96 ± 10	100 ± 10
	20°C	97 ± 7	100 ± 11

Deionised water	80°C	95 ± 10	100 ± 6
	20°C	98 ± 9	100 ± 9

The decrease in the tensile strength is very slight for all the conditions: it reaches only ~4% after one and half years aging at pH11 and 80°C. These strength losses are too small to be fitted. There is no significant influence of the pH on the tensile strength degradation, but it is slightly larger at higher temperature. Regarding the tensile modulus measured between 0.3 and 0.6% strain, it remains constant after one and half years aging under all conditions. It is known that the modulus of high performance fibres is governed by the chain orientations [14, 16, 17]. The chain scissions occurring during hydrolytic aging do not affect the tensile modulus, and thus the chain orientation.

4. Conclusion

Technora T240 fibres have been aged under alkaline conditions (pH9 and pH11) and in deionised water for up to one and a half years. Only slight chain degradation has been revealed at the surface for all the conditions, and bulk degradation has been noted only at pH9 and pH11. The surface state of aged fibres display some finish rearrangements, in the form of small aggregates at pH9 and in deionised water, and in the form of randomly oriented hexagonal shapes at pH11.

It appears that these evolutions do not affect the mechanical properties significantly. Indeed, the residual tensile strength is higher than 95% after one and half years aging under all conditions, and the tensile modulus remains constant throughout the aging duration.

The multi-scales analyses performed here have evidenced the high stability of *Technora* fibres in neutral and moderately alkaline conditions. From a “durability” point of view, the *Technora* fibres appear to be a suitable solution for alkaline ground reinforcement as replacement of less hydrolytically-resistant materials, such as polyester fibres.

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References

1. Benneton, J.-P., J.-C. Blivet, and M. Perrier. *Hydrolyse alcaline des géotextiles polyester (PET)*. in *Rencontres 97 Géotextiles et Géomembranes*. 1997. Reims.
2. Auray, G. and D. Simons, *Geotextiles:essential reinforcement.* JEC Composites Magazine, 2007(35): p. 58-61.
3. Blivet, J.-C., et al., *Renforcement par géosynthétique sur cavités potenielles: exemples de la déviation sud-ouest de Meaux (77)*, in *Rencontres géosynthétiques*. 2006: Montpellier (France).
4. Ferreira, *Etude des fibres et câbles haute performance en poly(p-phénylène-co-3,4’-oxydiphénylène téréphtalamide) (Technora) : Relation structure-comportement*

mécanique et recherche de critères de dépose de câbles. 1996, Université des Sciences et Technologies de Lille 1.

5. Imuro, H. and N. Yoshida. *Differences between HM-50 and PPTA-Aramides*. in *25th International Man Made Fibres Congress*. 1986. Dornbirn.
6. Mercier, J.P. and E. Maréchal, *Chimie des polymères: synthèses, réactions, dégradations*, in *Traité des Matériaux*, P.P.e.U. Romandes, Editor. 1993. p. 393-395.
7. Morgan, et al., *The hydrolytic degradation of Kevlar 49 fibers*, in *29th National sampe Symposium*. 1984.
8. Ozawa, S., *A new approach to high modulus, high tenacity fibers.* Polymer Journal, 1987. **19**(1): p. 119-125.
9. Saijo, K., et al., *Moisture sorption mechanism of aromatic polyamide fibres: diffusion of moisture into regular Kevlar as observed by time-resolved small-angle X-ray scattering technique.* Polymer, 1994. **35**(3): p. 496-503.
10. Derombise, G., L. Van Schoors Vouyovitch, and P. Davies, *Degradation of aramid fibres under alkaline and neutral conditions: relations between physico-chemical characteristics and mechanical properties*. To be submitted.
11. Derombise, G., et al., *Influence of finish treatment on the durability of aramid fibres aged under an alkaline environment* To be submitted.
12. Teijin, *Technora® - High Tenacity Aramid Fiber.*
13. Derombise, G., *Long-term behavior of aramid fibres in neutral, alkaline and marine environments*. 2009, Ecole Nationale des Ponts et Chaussées: Paris.
14. Northolt, M.G. and R. van der Hout, *Elastic extension of an oriented crystalline fibre.* Polymer, 1985. **26**.
15. Yeh and Young, *Molecular deformation processes in aromatic high modulus polymer fibres.* Polymer, 1999. **40**: p. 857-870.
16. Northolt, M.G., J.J.M. Baltussen, and B. Schaffers-Korff, *Yielding an hysteresis of polymer fibres.* Polymer, 1995. **36**(18): p. 3485-3492.
17. Northolt, M.G., *Tensile deformation of poly(p-phenylene terephtalamide) fibres, an experimental and theoretical analysis.* Polymer, 1980. **21**: p. 1199-1204.