

DURABILITY OF ARAMID GEOTEXTILES IN AN ALKALINE ENVIRONMENT

Guillaume Derombise¹, Laëtitia Van Schoors² & Peter Davies³¹ Laboratoire Central des Ponts et Chaussées, 75732 Paris Cedex 15, France. (guillaume.derombise@lcp.fr)² Laboratoire Central des Ponts et Chaussées, 75732 Paris Cedex 15, France. (laetitia.van-schoors@lcp.fr)³ IFREMER, French Ocean Research Institute, 29280 Plouzané, France. (peter.davies@ifremer.fr)

Abstract: Thanks to their high mechanical properties, geotextiles based on polyethylene terephthalate were still used a few years ago for ground reinforcement in an alkaline environment. However, because of premature ageing under these conditions (lime treated ground etc), this kind of polymer is today excluded for grounds where the pH exceeds 12. As a replacement solution, the geotextile producers have turned to polyaramid fibres, known for applications such as composite materials, ballistic fabrics in armour systems, ropes etc. These materials are suitable for ground reinforcement because of their high initial properties (Young's modulus, tensile strength, low density and high chemical resistance). However, there are few data on the durability of aramid fibres on account of their recent introduction. A few authors have studied the life time of these fibres when subjected to creep, tension-tension fatigue and thermal ageing. The hydrolysis and thermal-oxidation degradation mechanisms have been identified, but there is much less data concerning the effects of pH on the long-term behaviour of aramid fibres. Consequently, a study of the durability of aramid fibres in an alkaline environment has been carried out in order to improve understanding of the mechanisms involved in ageing. Accelerated ageing in basic solutions (pH9 and pH11) and at different temperatures (20, 40, 60 and 80°C) has been performed. Two materials have been studied: the *Technora T240* and the *Twaron 1000* fibres, both used in geotextiles. The chemical, physico-chemical and thermal characteristics as well as the surface state and the mechanical properties of the fibres at different ageing times have been followed.

Keywords: aramid, fibre, geotextile, ageing, long-term behaviour, alkalinity.

INTRODUCTION

Aramid reinforcement geotextiles have been developed for a decade, as one of the replacement solutions for PET geotextiles in an alkaline environment (lime treated ground etc). Indeed, it has been revealed that PET displays a premature ageing under basic conditions. Two aramid fibres which can be used for geotextiles are the Twaron and the Technora grades, both produced by Teijin. They differ in their chemical formula (Yang, 1989 and 1993) and their structure and morphology (Morgan et al., 1983, Panar et al., 1983, Dobb and Robson, 1990, Dobb et al., 1977, Rebouillat, 2001, Rebouillat, et al., 1997, Li et al., 1983 and Imuro, 1986). The Twaron fibres are based on poly(p-phenylene terephthalamide) (PPTA), Figure 1. The Technora fibres are based on copoly-(paraphenylene/3,4'-oxydiphenylene terephthalamide), Figure 1.

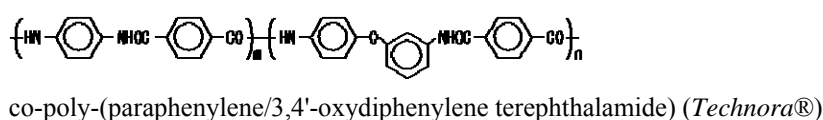
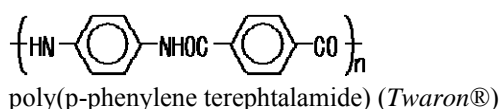


Figure 1. Aramid molecular structures

Depending on the grade of the Twaron fibres, the modulus has been measured to be between 78 and 123 GPa, the tensile strength between 2.8 and 3.6 GPa and the breaking strain between 2.5 and 3.5 % (Dobb and Robson, 1990, Yeh & Young, 1999 and Teijin (a)). These high mechanical properties, combined with a low density of 1.44 g/cm³ (Teijin (a)) and a high chemical resistance made the aramid geotextiles a serious candidate for ground reinforcement. In the same way, the Technora fibres modulus was found to be between 73 and 74 GPa, the tensile strength between 3.3 and 3.4 GPa, and the breaking strain between 4.5 and 4.7 % (Yeh & Young, 1999, Teijin (b)). The density of the Technora fibres is 1.39 g/cm³ (Teijin (b)).

Most of hydrolytical ageing studies reported in the literature refer to Kevlar fibres. As Twaron and Kevlar are both based on poly(p-phenylene terephthalamide), the hydrolysis mechanisms are similar. As presented by Morgan et al. (1984) the hydrolysis degradation of PPTA involves homolytic chain scission of the amide N-H linkage, yielding acid and amine functions. The authors established a relation that shows that the fibre strength degradation increases with time, temperature and applied load. They reported an average strength loss of 0.6% per year for unloaded fibres in a 100% relative humidity environment at 23°C, and of 12% per year in a 100% relative humidity environment at 65°C.

Auerbach (1989) studied the degradation kinetics of Kevlar 29 fibres, for different temperatures and humidities. The author identified two degradation mechanisms: a thermal-oxidative mechanism and a moisture dependent

mechanism. At 100% relative humidity, the moisture-controlled degradation was shown to be predominant almost to the exclusion of the thermal-oxidative degradation reaction. After identification and extrapolation at 25°C of the kinetics constants, the author predicted a 10% loss in strength after 25 years at both 10 and 100% relative humidity and 25°C. The loss in strength was close to 20% after 25 years exposure at 43°C.

Springer et al. (1998) followed the effects of basic and acid solution exposure (respectively 10% NaOH and 40% H₂SO₄) on mechanical properties of Kevlar 49 and Twaron 1055 fibres. Both modulus and tensile strength are affected under water-immersed ageing, but the properties drops are larger in acid and basic solutions than in neutral environment.

This article is an overview of the preliminary results from a study aimed at giving a better insight in the long term behaviour of aramid fibres aged in an alkaline environment. The analysis, characterisation and mechanical techniques employed will be described here. Morphology changes were also characterised. Some examples for Twaron 1000 fibres will be shown below, but it should be emphasized that this part of the work is ongoing and will continue for at least one more year.

EXPERIMENTAL AND PRELIMINARY RESULTS

Materials

Two materials have been considered for the present ageing study: *Twaron 1000* fibres in the form of 1680 dtex yarns, and *Technora T240* fibres in the form of 1670 dtex yarns. They are both produced by Teijin Aramid and employed in geotextiles for ground reinforcement. The former is glossy with a yellow colour; the latter is glossy and gold.

Ageing environments

Three different ageing conditions have been considered. Aramid samples were immersed in deionised water, and in carbonate sodium salt solution at pH9 and pH11 to study the influence of the pH on the degradation. The basic solutions are placed in beakers heated at 20, 40, 60 and 80°C in thermostated oil baths. In the same way, pure water thermostated tanks are heated at 20, 40, 60 and 80°C.

Tensile tests

Tensile tests have been performed using an Instron 4302 machine with a 500 N cell. The data were processed using Instron Series IX software. The gauge length (length measured between the clamps) was 500 mm; loading rate was 50 mm/min. During ageing the yarns were wrapped around cylinders and placed in water. The tests have been carried out on untwisted yarns at a relative humidity from 29 to 34% and at temperatures ranging from 22 to 24°C. Each trial was repeated at least 4 times.

So far tests have only been performed on the yarns aged in pure water tanks. An example of results showing the evolution of the tensile strength of the *Twaron 1000* fibres aged in pure water is given as an example on Figure 2. A drop of 30% of the breaking load is noted after 231 days in pure water at 80°C. The breaking load does not change after 231 days in pure water at 20°C.

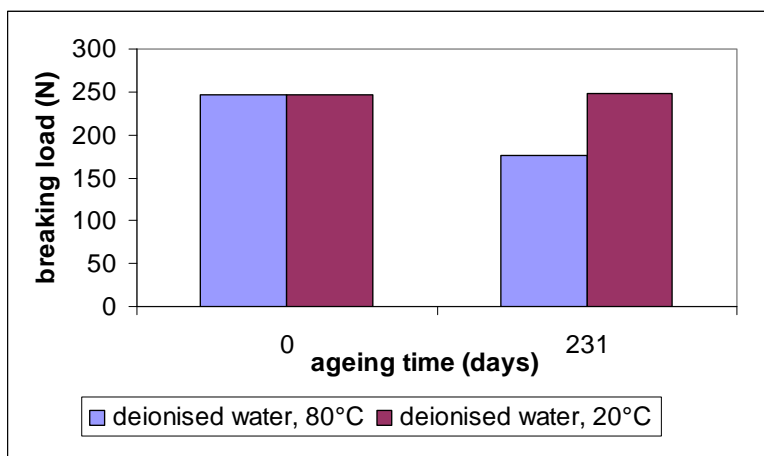


Figure 2. Evolution of the breaking load of *Twaron 1000* fibres aged in deionised water

Scanning Electron Microscopy (SEM)

Scanning electron micrographs of the fibres were performed to detect potential surface defects induced by ageing. The pictures were taken in the secondary electrons mode, at 12 kV voltage and at a working distance of 10 mm.

Some degradation features are visible as excoriations on the surface of *Twaron 1000* fibres aged at pH11 and 80°C for 364 days (Figure 3). These may be attributed to the removal of finish. No significant diameter decrease is observed after 364 ageing under these conditions.

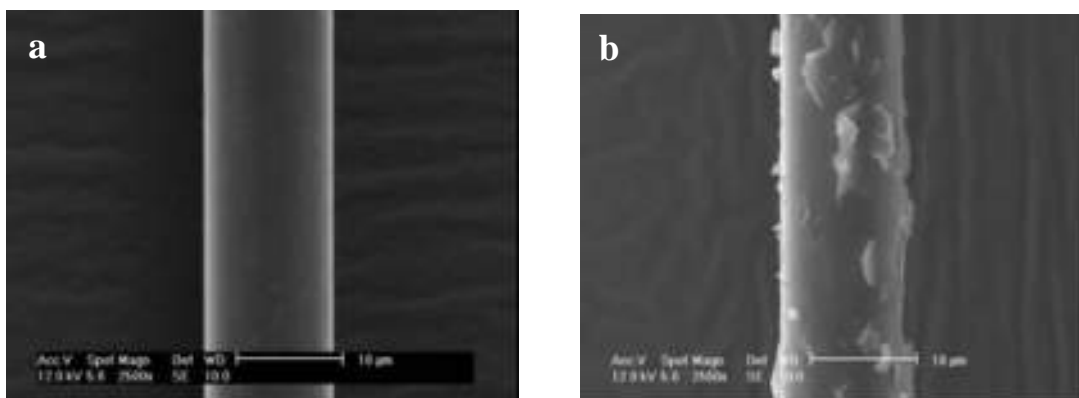


Figure 3. Scanning electron micrographs of *Twaron 1000* fibres (a) as-received, (b) after 364 days at pH11, 80°C

Fourier Transformed Infra Red spectrometry (FT-IR)

In order to follow the evolutions of chemical functions at different ageing times, the intensities of characteristic peaks were examined by Fourier Transformed Infra Red spectroscopy using a Diamond ATR (Attenuated Total Reflectance) apparatus. The spectra were obtained from a Nicolet impact 410 spectrometer. The data were processed using OMNIC 3.1 software. Fifteen fibres were taken for each test, which was repeated three times.

A peak related to the finish and located at 1109 cm^{-1} has been identified for *Twaron 1000* fibres. Another stable characteristic peak has been chosen to calculate the relative intensities: the peak located at $\sim 821\text{ cm}^{-1}$ related to the C-H deformation of aromatic rings (peak 1) appears to be appropriate. An example is given in Figure 4. A significant decrease of the intensity ratio is observed after 231 days at pH11 and 80°C. The ATR can thus be used to reveal significant finish loss under these ageing conditions.

The relative intensities of the amide functions characteristic peaks have also been followed as well for *Twaron 1000* fibres. The first one is located at $\sim 1634\text{ cm}^{-1}$ related to the C=O (peak 2), the second at $\sim 1538\text{ cm}^{-1}$ related to the combined motion of N-H bend and C-N (peak 3), and the last at 1307 cm^{-1} related to the C-N, N-H and C-C combined vibrations (peak 4) (Penn & Larsen, 1979). The hydrolytic degradation scheme of PPTA given by Morgan *et al.* (1984) would predict a decrease in amide properties, and an increase in acid and amine properties. After 231 days in pH11 solution heated at 80°C, only a slight decrease in the amide property of relative intensity from 1 to 5.5 % depending on the considered peak can be noticed. After 231 days under the other conditions, no clear trend can be drawn. An initial possible explanation of the observed stability of the amide characteristic peaks is that the macromolecules degraded at the surface of the fibres are soluble in the solution. Further aged samples will be analyzed to explore this.

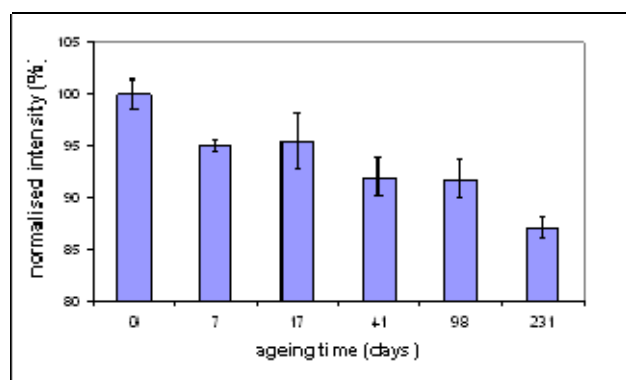


Figure 4. Relative intensity evolution of the peak related to the finish of *Twaron 1000* fibres aged at pH11, 80°C

Viscosimetry

Viscosity measurements show potential chains scissions. The Mark-Houwink relation given by Arpin and Strazielle (1997) in sulphuric acid concentrated at 96%, $[\eta] = 8 \times 10^{-3} \text{ M}^{1.09}$, enables the weight-average molecular weight to be followed with the ageing time. An Ubbelohde DIN capillary viscosimeter (*Schott Instruments*) is used. To calculate the inherent and the reduced viscosity, four concentrations have been chosen: $5 \cdot 10^{-4} \text{ g/mL}$, $1 \cdot 10^{-3} \text{ g/mL}$, $1.5 \cdot 10^{-3} \text{ g/mL}$ and $2 \cdot 10^{-3} \text{ g/mL}$. Higher concentrations were found to give poor repeatability of the measurements. The material is dissolved during 2 hours at 60°C under magnetic stirring.

The first results show an important decrease of the weight-average molecular weight of *Twaron 1000* fibres after 231 days in a sodium carbonate salt solution of pH11 at 80°C. Indeed, M_w goes from 31940 g/mol to 17310 g/mol after ageing. This reveals that hydrolysis and chain scissions do occur in the core of the fibres under exposure to basic conditions.

Density measurements

Density experiments were performed to study the development of porosity in the fibres. First 0.1 g of material was weighed at 20–23°C in ambient air. Then the fibres were weighed once immersed in dodecane, which appears to be inert and not absorbed by the *Twaron* and *Technora* fibres. The densities of air and dodecane are both known, so the density of the fibre can be calculated throughout the ageing period.

An example of results from the density measurements at different ageing times is displayed on Figure 5.

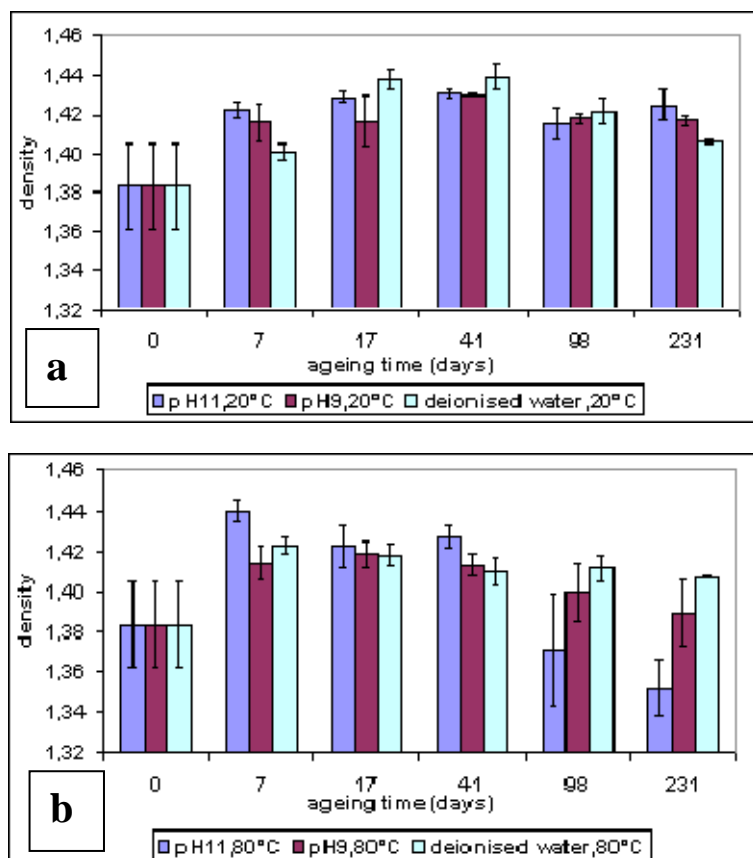


Figure 5. Density versus ageing time of *Twaron 1000* fibres immersed in deionised water, pH9 and pH11 solutions, at (a) 20 and (b) 80°C

For *Twaron 1000* fibres aged at pH11, the density first increases with ageing time from 1.38 to 1.43 g/cm³ after 41 days at 20°C, and from 1.38 to 1.44 g/cm³ after 7 days at 80°C. For *Twaron 1000* fibres aged at pH9, the density first increases with ageing time from 1.38 to 1.43 g/cm³ after 41 days at 20°C, and from 1.38 to 1.42 g/cm³ after 17 days at 80°C. For *Twaron 1000* fibres aged in deionised water, the density first increases with ageing time from 1.38 to 1.44 g/cm³ after 41 days at 20°C, and from 1.38 to 1.42 g/cm³ after 7 days at 80°C. These increases are interpreted as a predominant departure of finish, for which the density is lower than for the pure polymer, resulting in a global increasing of the density.

This correlates with the previous SEM observations. As the maximum of the density is reached sooner at 80°C than at 20°C, it can be affirmed that the finish loss is faster at higher temperature.

Next the density starts decreasing. For *Twaron 1000* fibres aged at pH11, it drops down to 1.35 g/cm³ after 231 days at 80°C, and to 1.42 g/cm³ at 20°C. This suggests that pore generation may be the prevailing phenomenon. All the same, the finish loss is continuous throughout the ageing under these conditions, as indicated by the previous FTIR results.

In the same way, for *Twaron 1000* fibres aged at pH9, the density drops down to 1.39 g/cm³ after 231 days at 80°C, and to 1.42 g/cm³ at 20°C. Finally, for *Twaron 1000* fibres aged in deionised water, it decreases down to 1.41 g/cm³ after 231 days at both 80°C and 20°C.

The effect of finish departure and pore generation on the evolution of the density can not be separated with this technique; the true porosity generation rate cannot be calculated from these first results.

Thermogravimetric Analysis (TGA)

Thermogravimetry continuously measures the mass of a sample subjected to a steady increase of temperature. It allows the change of the degradation temperatures, the remaining finish content and the absorbed water rate to be determined with the ageing time. The apparatus used was a NETZSCH STA 409. 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. An amount of 24.9 to 25.5 mg of material was weighed for each test. The measurement of the

equilibrium moisture of the fibre content was carried out by TGA. The thermograms were interpreted as displayed in Figure 6.

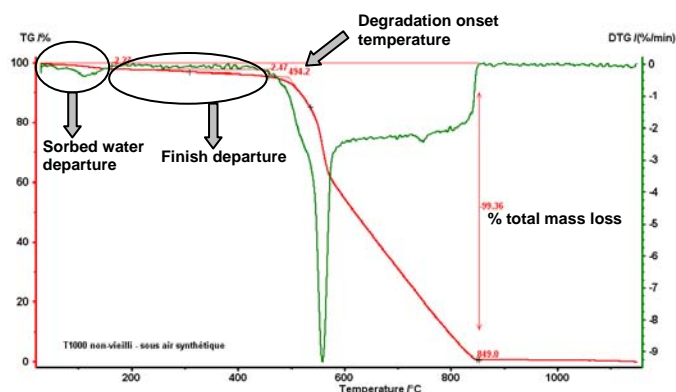


Figure 6. Profile and interpretations of the ATG thermogram obtained from the as-received *Twaron 1000* fibres

The amplitude of the first mass loss located between 25 and ~160°C depends on the storage conditions of the fibres. For the as-received *Twaron 1000* fibres, it goes from 2.27% in mass when stored with silicagel to 4.59% when stored at 55% relative humidity, at ambient temperature. The mass loss is thus attributed to the reduction of absorbed water. In the same way, the second mass loss located between ~160°C and the degradation onset temperature must be mainly due to the removal of finish, as it drops from 2.04% for as-received *Twaron 1000* fibres to 1.02% for as-received low finish content *Twaron 1010* fibres.

For *Twaron 1000* fibres, the first results show a decrease of the degradation onset temperature from 490 to 459°C after 231 days ageing at pH11 and 80°C, and from 490 to 484°C after 321 days ageing at pH9 and 80°C. At 20°C, the degradation onset temperature drops from 490 to 482°C after 231 days ageing at pH11, and from 490 to 482°C after 231 days ageing at pH9. The trend is similar for *Technora T240* fibres. The results are shown in Table 1. The decrease in the degradation temperature can be interpreted as the result of macromolecular chain failure, leading to the decrease of average molecular masses, and thus to smaller macromolecular segments which are degraded at lower temperatures. This interpretation is confirmed for *Twaron 1000* fibres aged at pH11 and 80°C by viscosimetry measurements.

Table 1. Degradation onset temperature change of aged *Twaron 10000* and *Technora T240* fibres.

Material	Degradation onset temperature (°C)
T1000, as-received	490
T1000, 231 days at pH11, 80°C	459
T1000, 231 days at pH9, 80°C	484
T1000, 231 days at pH11, 20°C	482
T1000, 231 days at pH9, 20°C	482
T240, as-received	462
T240, 231 days at pH11, 80°C	447
T240, 231 days at pH9, 80°C	447
T240, 231 days at pH11, 20°C	456
T240, 231 days at pH9, 20°C	446

Differential Scanning Calorimetry (DSC)

Analyses were performed in a DSC Q100 (*TA Instruments*). The TA Universal analysis software was used to process the data. The experiments were carried out under a nitrogen flow of 50 mL/min. About 10 mg of material were weighed in a hermetic aluminum pan. The sequence was as follows: the sample was heated from 0 to 400°C (below the degradation temperature) at 30°C/min. This high heating rate was chosen in order to increase the sensitivity of the analysis, as some of the observed transitions were hard to detect. Then it was stabilized at 400°C during 15 min in order to eliminate the thermal history of the material. Next it was cooled down to 0°C at 30°C/min. Finally, the sample was heated up to 400°C again at 30°C/min.

Particular attention was paid to the glass transition temperature, previously studied by Lafitte (1981) for PPTA fibres. The author noted a small transition around 300°C at 20°C/min under a nitrogen flow, attributed to the glass transition. The *Twaron 1000* fibre thermograms also display a small transition around 339°C (Figure 7). A very small increase of the transition temperature (around 1°C) is noted after 364 days at pH11 and 80°C. This could be attributed to a further recrystallisation, which would limit the mobility of non-crystallised macromolecular chains, resulting in an increase of the transition temperature. More work is needed to confirm this hypothesis.

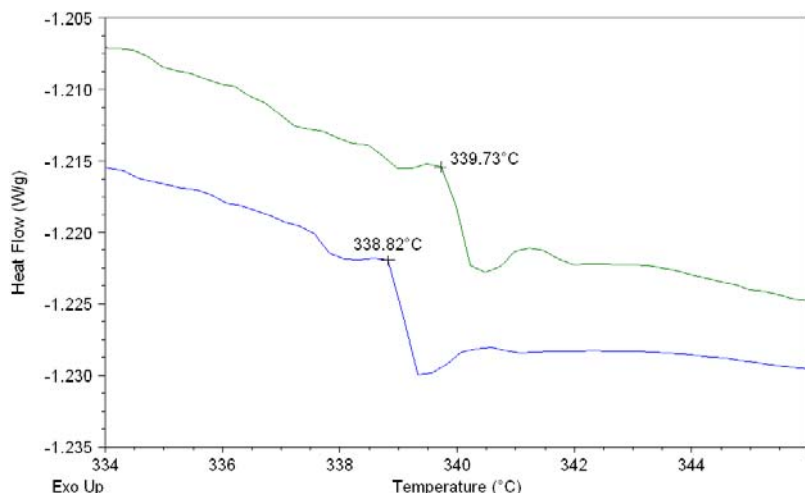


Figure 7. Transitions of *Twaron 1000* fibres: lower, as-received, upper, after 364 days at pH11, 80°C.

CONCLUSIONS

This paper presents first results from a study currently underway aimed at understanding and predicting the lifetime of aramid fibres employed as geotextiles in alkaline ground.

Finish removal was noted for *Twaron 1000* fibres aged at pH11 and 80°C, by Scanning Electron Microscopy, Fourier Transformed InfraRed spectrometry and density measurements. A study of the influence of the finish appears to be essential to determine how its removal affects fibre durability.

A decrease of 30% of the breaking load was observed for *Twaron 1000* fibres aged in pure water at 80°C. Under ageing at pH11 and 80°C, a decrease of the average molecular weight was revealed both by thermogravimetric analysis and viscosimetry, and porosity generation was followed by density measurements. Further work is required to explore the potential correlations existing between the mechanical properties and the physico-chemical characteristics.

Acknowledgements: The authors are grateful to Otto Grabandt and Bertil van Berkel of Teijin Aramid for the fibre samples and their cooperation.

The contributions of Dominique Duragrín and Béatrice Duchesne of LCPC, and Amaury Ducloux of IFREMER to density measurements, thermogravimetric analysis and mechanical testing respectively are also greatly appreciated.

Corresponding author: Mr Guillaume Derombise, Laboratoire Central des Ponts et Chaussées, 58, boulevard Lefebvre, Paris, 75732 cedex 15, France. Tel: +33 1 40 43 51 64. Email: guillaume.derombise@lcpc.fr.

REFERENCES

- Arpin, M. and Strazielle, C. 1977. Characterization and conformation of aromatic polyamides: poly(1,4-phenylene terephthalamide) and poly(p-benzamide) in sulphuric acid. *Polymer*, 18, 591-598.
- Auerbach, I. 1989. Kinetics for the Tensile Strength Degradation of Nylon and Kevlar Yarns. *Journal of Applied Polymer Science*, 37, 2213-2227.
- Dobb, M. G., and Robson, R. M. 1990. Structural characteristics of aramid fibre variants. *Journal of Materials Science*, 25, 459-464.
- Dobb, M. G., Johnson, D. J., and Saville, B. P. 1977. Supramolecular Structure of a High-Modulus Polyaromatic Fiber. *Journal of Polymer Science: Polymer Physics Edition*, 15, 2201-2211.
- Imuro, H. 1986. Differences between HM-50 and PPTA-Aramid. 25th International Man Made Fibres Congress, Dornbirn.
- Lafitte, M.-H. 1981. Caractérisation de la fibre aramide Kevlar 29: Etude du comportement et des propriétés mécaniques en tension et en torsion. PhD thesis (in French) Ecole Nationale Supérieure des Mines de Paris.
- Li, L.-S., Allard, L. F., and Bigelow, W. C. 1983. On the Morphology of Aromatic Polyamide Fibers (Kevlar, Kevlar-49, and PRD-49). *Journal of Macromolecular Science – Physics*, B22(2), 269-290.
- Morgan, R. J., Pruneda C. O., and Steele, W. J. 1983. The Relationship between the Physical Structure and the Microscopic Deformation and Failure Processes of Poly(p-phenylene Terephthalamide) Fibers. *Journal of Polymer Science: Polymer Physics Edition*, 21, 1757-1783.
- Morgan, R. J., Pruneda C. O., Butler, N., Kong, F.M., Caley, L., and Moore, R. L. 1984. The hydrolytic degradation of Kevlar 49 fibers. 29th National SAMPE Symposium.
- Panar, M., Avakian, P., Blume, R. C., Gardner, K. H., Gierke, T. D., and Yang, H. H. 1983. Morphology of Poly(p-phenylene Terephthalamide) Fibers. *Journal of Polymer Science: Polymer Physics Edition*, 21, 1955-1969
- Penn, L. and Larsen, F. 1979. Physicochemical Properties of Kevlar 49 Fiber. *Journal of Applied Polymer Science*, 23, 59-73.

- Rebouillat, S. 2001. Aramids, Ch 2 in High Performance Fibres, Ed. Hearle, Woodhead Publishing
- Rebouillat, S., Donnet, J.-B., and Wang, T. K. 1997. Surface microstructure of a Kevlar aramid fibre studied by direct atomic force microscopy. *Polymer*, 38(9).
- Springer, H., Abu Obaid, A., Prabawa, A. B., and Hinrichsen, G.. 1998. Influence of Hydrolytical and Chemical Treatment on the Mechanical Properties of Aramid and Copolyaramid Fibers. *Textile Research Journal*, 68 (8), 558-594.
- Teijin Ltd., (a) Specification, Twaron, the Power of Aramid – Twaron for Heat and Cut Protection.
- Teijin Ltd., (b) Specification, Technora – High Tenacity Aramid Fiber.
- Yang, H. H. 1989. Aromatic high strength. Wiley interscience Ed, 226-289.
- Yang, H. H. 1993. Kevlar Aramid Fiber. John Wiley & Sons Ed.
- Yeh, W.-Y, and Young, R. J. 1999. Molecular deformation processes in aromatic high modulus polymer fibres. *Polymer*, 40, 857-870.