Ageing of high performance polymers used in civil engineering: polyester and aramid geotextiles

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ABSTRACT: A few years ago, polyester fibres were widely used for civil engineering applications such as ground reinforcement, because of their good mechanical properties. However, considering their premature ageing in alkaline environment, the use of this chemical nature of polymer is nowadays excluded in grounds where the pH is superior to 12 and not advised for pH exceeding 9. Alternative high mechanical performance fibres have been thus proposed, among which are polyaramide fibres. This study aims at comparing the evolution of the functional properties, that is to say mechanical properties (more specifically the residual tensile strength and the residual stiffness) of polyester and of two types of polyaramides aged in moderately alkaline environments (pH9 - pH11). These results highlight that the residual stiffness decreases strongly for polyesters whereas it is preserved for aramid fibres even after one and half years in the most aggressive conditions (pH11 and 80°C). As for the residual tensile strength, significant falls are observed for polyester and PPTA fibres whereas minor decreases are revealed for Co-PPTA-ODP fibres. These differences can partially be explained by different degradation mechanisms revealed by physico-chemical, micro-structural and morphological characterizations.

1 INTRODUCTION

For nearly half of century, poly(ethylene terephthalate) (PET) fibres have been used in geotextiles for reinforcement applications because of their good mechanical properties associated with a “low” cost. However, these fibres are sensitive to hydrolysis. This involves chain breaks of ester linkages that generate alcohol and acid functions (Bellenger et al., 1995) (Fig. 1).

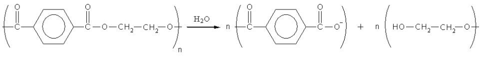


Figure 1: Hydrolysis of polyester

The kinetics is slow in neutral environment and accelerated in basic environment. For example, Elias et al. (1998) highlighted for different polyester grades that, at 20°C, the tensile strength decreases by 0.06% to 0.31% per year at pH7, by 0.35% to 0.77% per year at pH10, and by 4.10% to 25% at pH12. The assessed lifetime could therefore vary from more than a century at pH7, down to a few years at pH greater than 12. So, the use of PET geotextiles for applications requiring a long lifetime in alkaline environment must be avoided for pH exceeding 10, and is prohibited for pH exceeding 12 (Benneton et al., 1997).

Henceforth, geotextiles based on aramid fibres, which have been used for a decade for soil reinforcement (Auray and Simons, 2007; Blivet et al., 2006), are being proposed as a possible replacement solution for polyester geotextiles in alkaline environments. The higher cost of this polymer limits therefore their generalization. Moreover, it has been shown that these polymers are also subjected to hydrolysis (Fig. 2) in aggressive alkaline solutions (Springer et al., 1998). The reaction involves a scission of the amide C-N linkage to generate amine and acid chain-end functions.

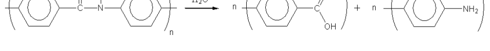


Figure 2: Hydrolysis of polyaramid

Imuro and Yoshida (1986) have compared the mechanical properties evolutions of aramid fibres based on poly(*p*-phenylene terephthalamide) (PPTA) and copoly-(paraphenylene/3,4’-oxydiphenylene terephthalamide) (Co-PPTA-ODP) in very basic environments and at high temperatures. The authors reported that the tensile strength of Co-PPTA-ODP fibres decreases by 25% after 100 hours in a 10 wt% NaOH solution at 95°C, whereas in the same conditions, the tensile strength of PPTA fibres decreases by 80%. However, the long-term behaviour of aramid fibres in moderately alkaline conditions (pH9 to pH11) would need to be further explored.

This paper gives a comparison of the tensile properties evolutions of different commercial fibres used for ground reinforcement, namely PET fibres and two aramid fibres, aged in moderately basic conditions. The different behaviours will also be explained from a microstructural and a morphological point of view.

2 MATERIALS AND METHODS

2.1 *Materials*

The PET fibres are in the form of woven geotextiles with a tensile strength of 100 kN/m. Two types of aramid fibres manufactured by Teijin Aramid were analysed: *Twaron 1000* (1680 dtex), based on poly(*p*-phenylene terephthalamide) appointed PPTA, and *Technora T240* (1670 dtex) which is a copolymer based on copoly(paraphenylene/3,4'-oxydiphenylene terephthalamide) appointed Co-PPTA-ODP.

2.2 *Ageing methods*

Two ageing conditions were considered in this study. PET and aramid fibres were immersed in solutions of sodium carbonate salt at pH9 and pH11. A wide range of ageing temperatures was studied but results discussed in this paper focus on 45 and 75°C for PET fibres, and 40 and 80°C for aramid fibres.

2.3 *Mechanical tests*

Tensile tests were performed on single fibres using a Zwick 1474 tensile testing machine, at 20 ± 1°C. The average diameter of the fibres was measured before each test with a laser micrometer Mitutoyo LSM-500S. Around 30 tests were performed for each time and ageing condition. In order to characterize the real evolution of the mechanical characteristics during ageing, the residual strength and the residual stiffness were expressed in Newtons and then normalised with respect to the initial value.

3 TEST RESULT AND DISCUSSION

3.1 *Residual tensile strength*

Figure 3 shows the variation of the residual tensile strength of polyester and aramid fibres as a function of ageing time, respectively at pH9 (a) and pH11 (b), for the highest temperatures.

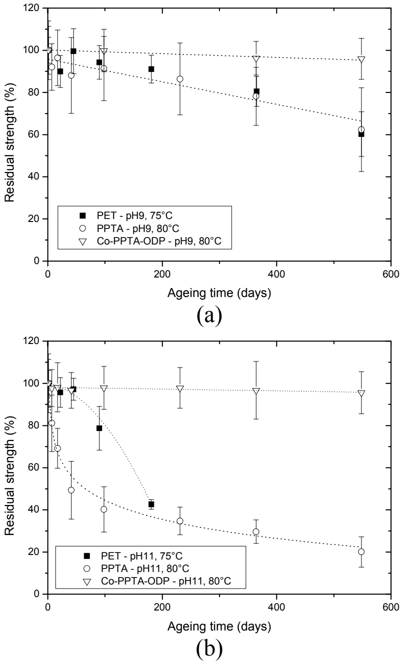


Figure 3: Residual tensile strength evolution of PET and aramid fibres respectively aged at 75°C and 80°C (a) at pH9 and (b) at pH11

The residual tensile strength depends strongly on the pH and on the nature of the fibres. Actually, for Co-PPTA-ODP fibres, the tensile strength decreases less than 5% even after one and half years ageing for all conditions. This high stability is in accordance with the previous physico-chemical analyses which revealed only some slight surface hydrolysis and possibly few bulk degradation (Derombise et al., 2009b).

Concerning PET and PPTA fibres, the residual tensile strength decreases with ageing time. Moreover, these decreases are more important at pH11 than at pH9. The pH has thus a strong influence on the residual tensile strength evolution.

At pH9 (Fig. 3a), the residual tensile strength decreases as a linear function with ageing time in the same proportion for both PET and PPTA fibres. For the latter, the drop in the residual tensile strength is significant (≈ 40%) after one and a half years at pH9 at these temperatures (80°C for PPTA and 75°C for PET). At lower temperatures (40°C for PPTA and 45°C for PET), the tensile strength is less affected: the decrease reaches 10% for PET and 30% for PPTA fibres.

It has been shown previously that the decrease in the residual tensile strength of PPTA fibres could be attributed, at pH9, to the degradation of transversal “links” (such as tie-molecules and tie-fibrils) and to the development of porosity (Derombise et al., 2009a and Derombise, 2009c). For PET, this decrease could be ascribed, at pH9, to the drop in the polymer chains average molecular mass.

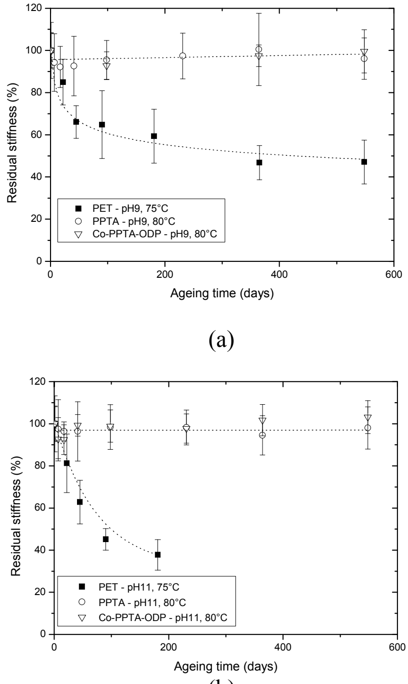
At pH11, the evolutions of the residual tensile strength appear to be different for PET and PPTA fibres (Fig. 3b). Indeed, the residual tensile strength decreases with ageing time as a linear function for PET fibres and as a logarithmic function for PPTA fibres. It may be noted therefore that the PET fibres become too brittle to be tested after 6 months of ageing at pH11 and 75°C.

It has been highlighted in a previous study that the logarithmic evolution observed for PPTA fibres may result from two decay processes at pH11, namely the degradation of tie-molecules/fibrils and the degradation of the crystallites (Derombise et al., 2009a and Derombise, 2009c). In a similar way, it has been reported that the drop in the residual tensile strength of PPTA fibres is larger at pH11 than at pH9 mainly because of the more numerous chain scissions highlighted by viscosity analysis (Derombise et al., 2009a).

For PET fibres, the drop in the residual tensile strength can be attributed partially to the decrease in the average polymer chains molecular mass but especially to the reduction of the diameter of fibres (Van Schoors et al., 2008) (Haghighat Kish and Nouri, 1999). Indeed, SEM observations on the fibre sections show that the diameter of PET drops ~25% after only 6 months ageing at pH11, and it remains constant after one and half years ageing at pH9 at 75°C. Thus, the chemical degradation of PET fibres mainly takes place at the surface at pH11. On the contrary, at pH9, it appears that the degradation occurs exclusively in the bulk of the fibre. For PPTA fibres, similar trends are also observed. So it has been shown the development of an open porosity in the outer regions at pH11 and a closed porosity at pH9 (Derombise, 2009c). However, this does not induce any reduction in the fibre diameter.

3.2 *Residual stiffness*

Figure 4 shows the variation of the normalized residual stiffness of PET and aramid fibres at 75°C and 80°C respectively, as a function of ageing time for the two pH. The stiffness has been measured between 2 and 4% deformation for polyesters, and between 0.3 and 0.6% deformation for aramids, corresponding to the deformation range of fibres in usual application.



(a)

(b)

Figure 4: Residual stiffness evolution of PET and aramid fibres respectively aged at 75°C and 80°C (a) at pH9 and (b) at pH11

At pH9 and pH11, the evolution in the residual stiffness strongly depends on the chemical nature of the fibre (Fig. 4a and 4b). For aramid fibres (PPTA and Co-PPTA-ODP), the residual stiffness remains constant whatever the ageing conditions. According to Northolt et al. (1980) and Northolt et al. (1985) the tensile modulus of aramid fibres is mainly associated to the crystallites orientation. Consequently, the hydrolytically degradation in alkaline environment does not generate any crystallite disorientation or aramid chains decohesion (Derombise et al., 2009a and 2009b).

Concerning the PET, the residual stiffness drops about 40% after one and half years at pH9 and 75°C, and about 60% after 6 months at pH11 and 75°C.

At pH9 this decrease may result in the decrease of the average polymer chains molecular mass, favouring decohesion between the chains in the polymer matrix. At pH11, the reduction in the residual stiffness may result from the degradation of the polymer chains and especially from the decrease in the fibre diameter. However, at 45°C, the decreases are less important but all the same worrisome. Indeed, they are about 10% at pH9 and 20% at pH11, after one and half years.

According to this study, aramid fibre uses constitute an improvement for the conservation of the residual stiffness at pH 9 and pH 11. The physico-chemical modifications induced by alkaline ageing underlines that the same causes do not necessarily produce the same effects on the fibres stiffness. Indeed, at pH 9, the mutli-scale analyses of PET and PPTA aged fibres reveal that the main degradations are related to the decrease of the average molecular mass. However, for the semi-crystalline PET fibres (Xc = 42%), the chains breaks favour decohesion in the polymer matrix, which strongly affect the fibres residual stiffness. On the contrary, for crystalline aramid fibres, (considered as 100% crystalline), these chains cleavages do not entail re-orientations or decohesion between chains, and thus have no consequences on the residual stiffness. The results show that the microstructural specificities of fibres govern their intrinsic properties but also their evolution with time.

4 CONCLUSION

In this study, the long term behaviour of aramid and polyester fibres in a moderately alkaline environment have been compared. The evolutions in the functional properties, more specifically residual strength and residual stiffness, have been determined and correlated with physico-chemical, microstructural and morphological characteristics modifications.

For PET fibres, the residual tensile strength decrease in alkaline environment. This decrease has been attributed to chain cleavage at pH9, associated to a reduction in diameter at pH11. Moreover, the residual stiffness seems to be affected by chains breaks, favouring a decohesion in the polymer matrix.

For aramid, the behaviour in alkaline environment is rather different as the specificity of the fibre. So, for PPTA, the residual tensile strength decrease in alkaline environment. For this fibre, this decrease has been attributed to only chain scission at pH11, and to chain cleavages and to the development of a closed porosity at pH9. Despite the chain scissions, the stiffness remains constant because of the particular microstructure of these fibres (Xc≈ 100%). Finally, for Co-PPTA-ODP fibres, the mechanical characteristics remain stable at pH 9 and 11. According to multi-scale analyses, these fibres seem thus not or little sensitive to the phenomena of hydrolysis in these aggressive environments until one and a half years of ageing.

Considering this study, Co-PPTA-ODP fibres appear to be a good solution, for reinforcement applications in treated soils in terms of durability.

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