EXHAUSTIVE LONG-TERM STUDY ON HYDROLYSIS OF HIGH-TENACITY POLYESTER - 10 YEAR RESULTS

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Abstract: The hydrolytic degradation of high-tenacity polyethylene terephthalate (PET) yarns has been investigated using a long-term experimental study. The aim of this work is to understand and model the chemical resistance of high-tenacity polyester yarns used in mechanically stabilized earth structures. Thus, an experimental program, divided in three parts, has been carried out: (1) Immersion of high tenacity fibres for 3 months in 27 different media at 95°C; (2) Exposition of 5 different yarns at 80°C to 3 media (water pH 7, hydrochloric acid pH 1 and caustic soda pH 12) for more than 500 days; (3) Still running are experiments on high tenacity yarns exposed at 23 and 50°C in four different media (water pH 7, hydrochloric acid pH 1, caustic soda pH 12 and saturated lime pH 13) for 15 years. The evolution of the strength loss has been followed, comparing the effect of media and time on PET hydrolytic rate. The results of this program suggest a new approach for the modelling of PET hydrolytic degradation in water: we can consider a time-lag before actual loss of strength starts, followed by a constant degradation rate. The activation energy of both parts of the degradation process can be shown to be the same and follows the Arrhenius equation allowing anticipation of the strength loss of PET yarns in neutral environments with various times and temperatures.

Keywords: Polyester, durability, lifetime prediction, temperature, reinforcement, geosynthetic.

INTRODUCTION

High tenacity poly(ethylene terephthalate) (PET) yarns is used in mechanically stabilized earth structures for several decades. They are obtained by the polycondensation of a diacid (terephthalic acid) and a dialcohol (ethylene glycol) as shown on figure 1.
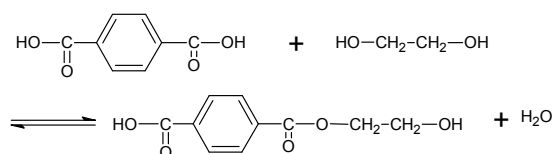

Figure 1. Degradation of PET by hydrolysis

This reaction is reversible when the polymer is in contact with water molecules: the hydrolysis of high tenacity PET yarns leads to statistical chain-scission resulting in mechanical strength loss (Launay *et al.*, 1999; Ballard *et al.* 1989). The hydrolysis rate of PET yarns depends on the temperature and pH. As an example, the degradation mechanism in high pH (caustic soda) is different from the one presented above. Indeed, this last reaction is catalyzed by hydroxide ions (OH^-) and hydrogen ions (H^+), respectively present in basic and acidic media.

The kinetic of PET hydrolytic degradation has been studied by many authors, based on accelerated and short period tests. In 1990, a specific program launched at Texas Research International by *Terre Armee Internationale* has been developed to study the hydrolytic degradation of polyesters during more than 10 years. This program is still running and the results are regularly reported in order to understand the different steps of polyester hydrolytic degradation. Thus, the important amount of data collected during 10 years has been used to make a synthesis and propose a scheme, a new model to determine the hydrolytic degradation rate at various time and temperature.

This paper is focused on two main orientations:

- Degradation in water (pure, neutral, salty)
- Degradation in caustic soda, lime and acidic solutions, known to be aggressive for PET, which are not suitable for long-term application.

The aim of this procedure is to develop a new kinetic model concerning the hydrolytic degradation of PET fibers based on long-term durability study.

TESTING PROCEDURE

For the first part of the study, PET yarns have been exposed to 25 solutions (including pure water, salty water and various pH levels solutions) during 80 days at 95°C (temperature at which the CEN test on hydrolysis is performed). The second part included various PET yarns exposed at 80°C, to observe the hydrolysis mechanism of various sources of material and selected solutions (pH = 7). In the third part of this research program, high tenacity PET fibers have been exposed to different media (1<pH<13) during 10 years, at 23°C and 50°C, to understand the effect of pH and (soil) temperature on the material strength, currently used in geosynthetics for soil reinforcement. During these experiments, the yarns have not been exposed to light. For each yarn, samples have been retrieved and mechanically

tested by uniaxial traction machine. The properties measured (strength and elongation at break) have then been compared to the initial properties.

RESULTS AND DISCUSSION

Experimental

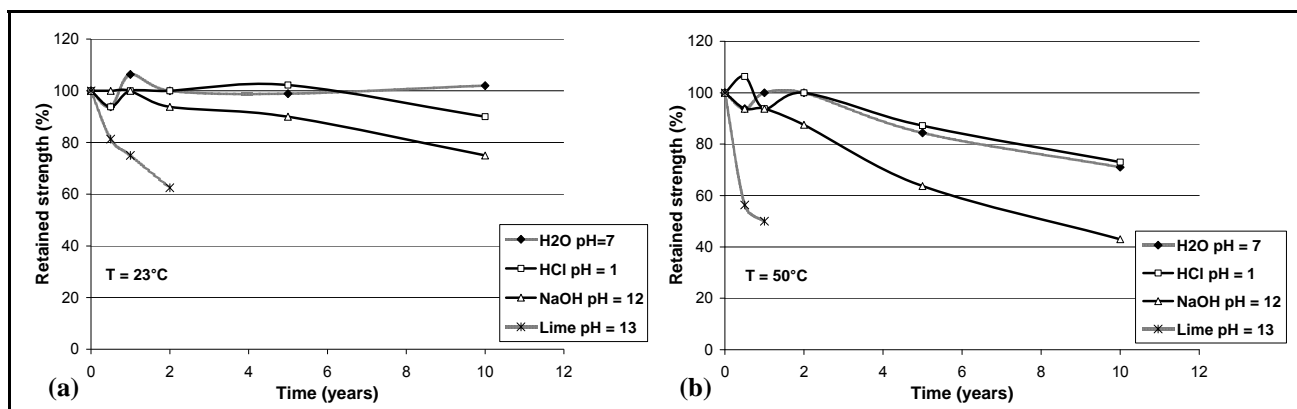The evolution of PET strength loss with time, temperature and pH is presented figures 2a and 2b.

Figure 2. Hydrolytic degradation of PET filaments in various media (1<pH<13) at (a) 23°C and (b) 50°C during 10 years

These figures show an increase of the degradation rate with temperature: the hydrolysis of PET is accelerated when the temperature increases. The strength loss is also highly dependent on media nature. If the average evolution of strength loss is the same during the first 2 years, it diverges after this period for caustic soda and lime. The degradation process in these media, as expected, is a catalyzed hydrolysis coupled with surface erosion that leads to the material embrittlement: the hydroxide ions (OH^-) catalyze the hydrolysis of the yarn, but it erodes the material surface by modifying its dielectric properties. This modification is equivalent to a chemical barrier against the penetration of the hydroxide ions into the yarns. Both media are more aggressive than the others. In saturated lime, the strength loss becomes critical even at ambient temperature, this alkaline media being more aggressive than caustic soda (the pH of the solution is as important as the chemical composition of the base considered).

That's why it is not recommended to use PET geosynthetics reinforcements in contact with lime stabilized embankment or in contact with concrete.

Figure 3 presents the loss of tensile strength according to pH value at 95°C (Jailloux *et al.*, 1992). We observe that strength loss increases between 10 and 12 pH. Thus, in alkaline media the hydrolysis rate of the polymer is highest than in pure water or acidic solution. This is due to another degradation process in this media as explained above.
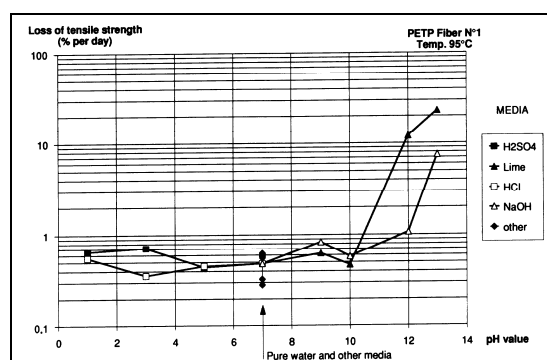

Figure 3. Hydrolytic degradation of PETP filaments in various media (1<pH<13) at 95°C

The global evolution of hydrolysis rate in neutral media is presented figure 4. The degradation evolution with time can be described in 3 parts:

- *Phase 1 (time-lag)*: the polymer tensile strength is stable or sometimes increases slightly because of chemicrystallization (Allen *et al.*, 1991). This last phenomenon can be explained by chain-scission (due to hydrolysis in the amorphous phase of the polymer) that leads to the disentanglement of chain segments. The rearrangement of these short molecules induces an increase of crystallization rate (chemicrystallization) hence a slight increase of the tenacity. That can be measured by Infrared Spectroscopy or density analysis (Jailloux *et al.*, 1990).
- *Phase 2*: the hydrolytic degradation rate is stable until 50% of loss.

- *Phase 3:* beyond ≈ 50% of strength loss, we do not observe a dramatic drop of the degradation rate as it was anticipated by an autocatalytic scheme. On the contrary, the degradation rate decreases. That can be attributed to the fact that degradation in crystalline phase is slower than in amorphous phase and that during the degradation process, the crystalline phase proportion increases in the total matter.
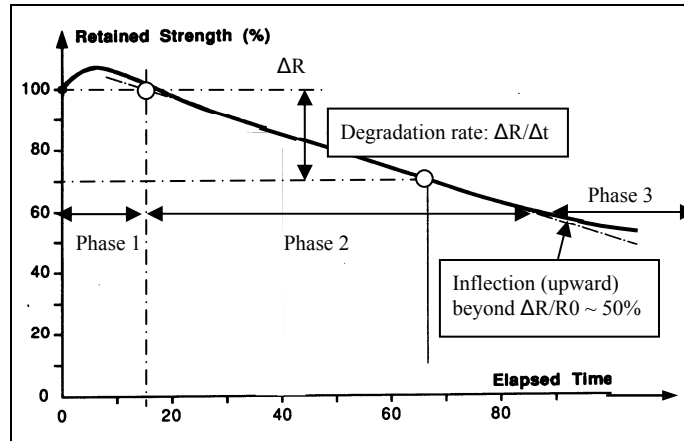

Figure 4. General hydrolytic degradation evolution with an incubation period followed by a constant rate

As shown in figure 5, a correlation has been found between carboxylic end groups (CEG) count and the inverse of the molecular weight, for degraded fibers. So we can use both parameters to characterize the fiber hydrolysis, except in caustic soda concentrated solution (pH = 13, non-linearity due to erosion as explained previously).
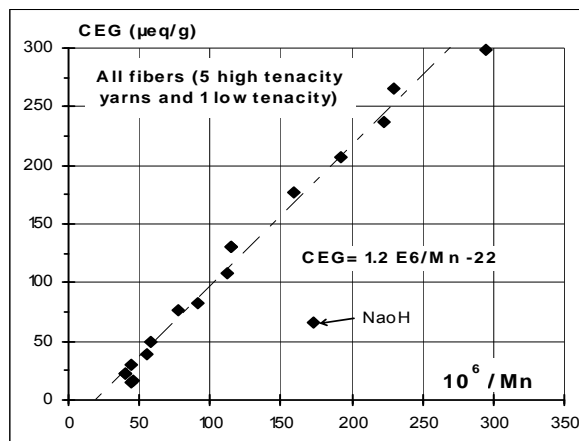

Figure 5. The CEG count depends on the inverse of the molecular weight for various degraded yarns

The following figures 6, 7 and 8 present the evolution of residual strength with time in different media and at respectively 95, 80 and 50°C (associated with the results obtained at 23°C). From these curves we extracted the two parameters of our general degradation curve (figure 4): the incubation time and the slope of the degradation curve.
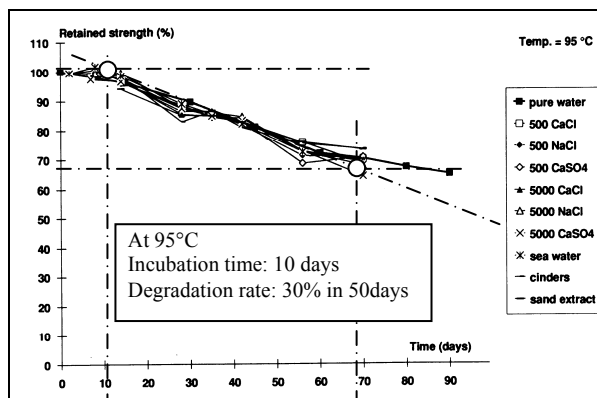

Figure 6. Degradation curves at 95°C for various media including pure water, salty waters and sea water
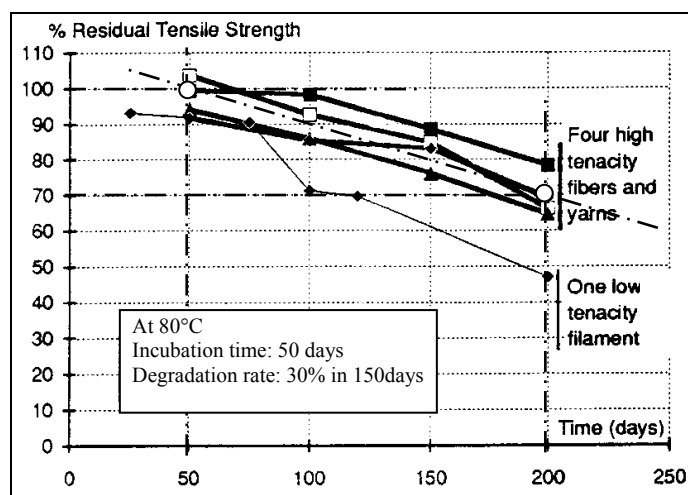
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Figure 7. Degradation curves of 5 products at 80°C in water (Anderson *et al*, 1992)
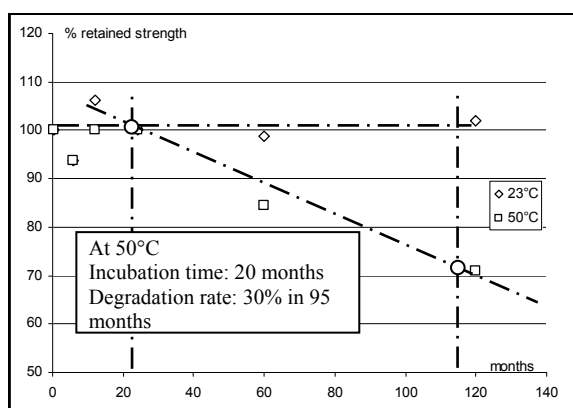

Figure 8. Degradation curves at 50°C in water; at 23°C the points are still in the time-lag

As expected, the strength loss increases with temperature in neutral media. We observe that there is no effect of salty ions on PET hydrolysis. At 80°C we have retained an average value for the four high tenacity yarns. The curves differ mainly by the time-lag (phase 1), not by the slope of the degradation curve. So, for each temperature considered, the global evolution of hydrolysis is the same.

Modeling

Figure 9 presents a comparison between the direct straight degradation line, used by most authors, and our proposal to separate the time-lag and the further degradation. As expected, the slope in the latter case is more pronounced, the location of the crossing of the two models depends on the degradation conditions (temperature, media, etc.).
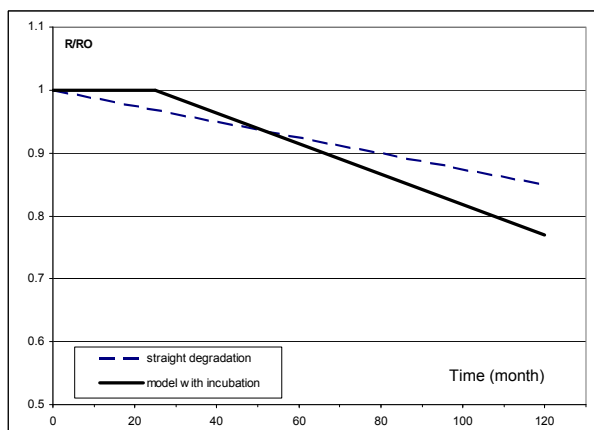

Figure 9. Model of degradation with or without incubation period

Now, one must assess whether the Arrhenius equation can be applied both to the degradation time (in fact the inverse of time) and the slope. Figures 10a and 10b present respectively the Arrhenius plot for the time-lags and for the degradation rates observed at 95°C, 80°C and 50°C. We observe that both activation energies are similar. The average value we suggest is 21 350 cal/mole, which is significantly lower than the value generally retained, around 25 000 cal/mole.
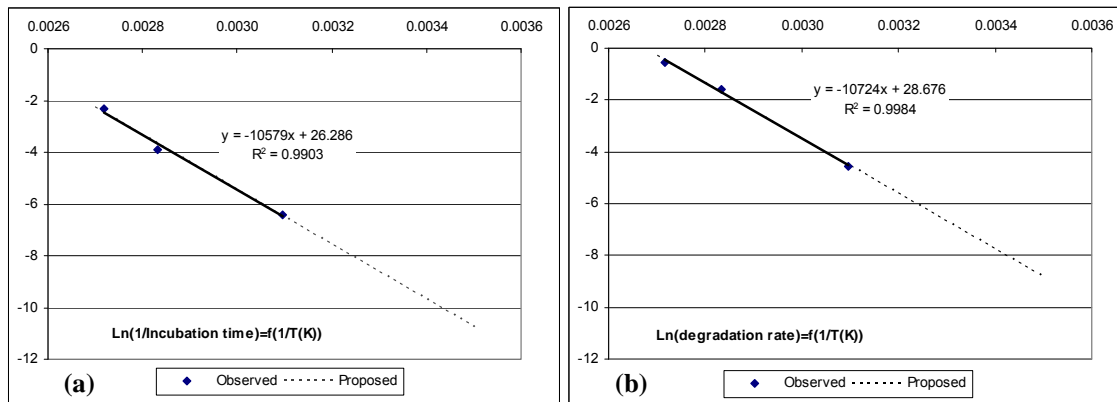

Figure 10. Arrhenius plot for (a) the inverse of time-lag and for (b) the degradation rate

Hence the expression of the time-lag in function of temperature, after adjusting the curves:

$$I_t \, (\text{days}) = 1/e^{(26.6 - 21350 / 2 \, T_K)}$$

With 2 being the value of R (= 2 cal/mol.K), the perfect gas constant, and T_K is the absolute temperature.

At 95°C the time-lag is 11 days; it becomes 35 years at 23 °C and this is the reason why no degradation at all, or even a slight strength increase, can be seen for many years at ordinary temperature.
And the expression of the degradation rate is

$$R_{deg} \, (\%/\text{day}) = e^{(28.5 - 21350 / 2 \, T_K)}$$

This rate varies from 0.6 %/day at 95°C (beyond 11 days) to 0.19 %/year at 23°C (beyond 35 years).

Other experiments can be compared to the model. For example, hydrolysis test on bare yarns at 70°C in water (Elias *et al*, 1998) give a retained strength of about 60 % after 665 days; the model gives 58.4 %.
The CEN test (EN12447) recommends 28 days at 95°C, which, according to the model, leads to a degradation of 10 %, indeed the value obtained by the manufacturers of PET webbing. So this work shows that the actual recommendations of the CEN test can be modified to lowest temperature (80°C for example) if the relation between the 2 first phases of hydrolysis (time-lag and degradation slope) and temperature are known.

It is most probable that the time-lag is a parameter sensitive to the conditioning of the yarn, its surface treatment if any or any kind of protection as commented above. On the contrary, more likely the rate of degradation due to the nature of the molecule should be rather independent from the yarn source. The modification of PET yarn surface has a real impact on the water diffusion into the material, thus on the Arrhenius parameters of the time-lag phase.

CONCLUSION

The extensive experimentation conducted by *Terre Armée Internationale* on hydrolytic degradation of polyester yarns has allowed a new model to be proposed in which
- First, the hydrolysis phenomenon does not lead to a strength decrease during an incubation period,
- Second, the yarn is submitted to a constant rate of degradation at least up to 50 % of retained strength.

Both parameters (inverse of time of incubation and degradation rate) depend on temperature according to Arrhenius equation in which the activation energy is set at 21 350 cal/mole.
This new approach allows computing the strength degradation expected at any time and temperature for applications in neutral environment.

Concerning long-term results (10 years), they lead to a reconsideration of PET use in geosynthetics: the temperature is an important parameter in the hydrolysis process. So, in high soil temperature (T°C > 35°C), the polyester is more sensitive to hydrolysis. So, taking into consideration the results of the present study, it seems necessary to (re-) define precisely the temperature in the structure calculation when they are reinforced with PET geosynthetics. In addition, it should be interesting to develop a testing method where PET yarns were aged in real conditions (not totally immerged in water) to re-evaluate the reduction factors used in design strength calculation in the case of polyester geosynthetics.

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