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Long term testing of polyester yarn and product at 50°C and 23°C in different environments

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ABSTRACT : The kinetics of the hydrolysis of polyester yarns used in geosynthetics is progressively better understood, thanks to temperature accelerated testing. The paper recalls the different phases of the research program launched in 1990 by Terre Armée Internationale. After the findings of the previous steps performed at elevated temperatures (95°C and 80°C), the paper presents the initial results of the third and long-term phase, at 50°C and 23°C. Now, after only two years, only the tests conducted in an extremely aggressive media can be usefully investigated. They suggest that two different Arrhénius coefficients might have to be considered in the kinetics of hydrolysis above and below the glass transition temperature. This results in practical consequences for current designs, identified at the end of the paper.

1. INTRODUCTION

In 1990, after Terre Armée Internationale concluded that Polyester Terephtalate (PETP) was a better candidate for permanent soil reinforcement applications than other polymeric materials, they launched an original research program devoted to the long-term performance of PETP fibres used in geotextiles and related products. A particular emphasis was placed on hydrolysis (the specific mechanism of degradation of this material) and on the related kinetics.

This article recalls the main findings of the previous phases and presents the first results of the third phase : study of the mechanical degradation of one high tenacity yarn and the corresponding finished product, at two temperatures (50°C and 23°C) in four different media (water, HCl pH1, NaOH pH12 and saturated lime to simulate fresh concrete). The results after two years are presented and discussed.

The final section of the paper presents some practical consequences which can already be drawn from the earliest results of the third phase, regarding civil engineering practice and the design of structures using polyester based reinforcements.

2. PRESENTATION OF THE PROGRAM

The program was divided into three phases, each of them with a particular purpose.

2.1 *First phase*

The first phase is completed. One specific high tenacity fibre, was immersed for up to three months in 27 different media, at 95°C, in order to establish for the first time the experimental relationship between the pH of the medium (ranging from 1 to 13) and the rate of hydrolysis, as well as the influence of major chemical components found in the soil. Strength and strain retention at break were measured on filaments (30 replicates).

2.2 *Second phase*

The second phase is also completed. Five distinct yarns, including the one tested in Phase 1, were exposed at 80°C to 3 contrasted media. The media were water (pH 7), HCl (pH 1) and caustic soda (pH 12). The yarns were four different high tenacity yarns and one low tenacity fibre. This phase lasted more than 500 days. Numerous assessment tests were completed in addition to the mechanical tests : 16 selected yarns were subjected to the following investigations :

- density, with an accuracy of 0.1 kg/m^3
- Mn, Mw, Mz, three different molecular weights, determined by the gas permeation chromatography technique (GPC) with a plot of the distribution curve
- carboxyl end group count (CEG).

2.3 *Third phase*

The third phase is now underway. It is meant to last about 15 years. One high tenacity yarn and one finished product using the same yarn are exposed at 50°C and 23°C in four different media : water (pH 7), HCl (pH 1), NaOH (pH 12) and saturated lime (pH 13) to simulate fresh concrete. The product is a geogrid obtained by weaving the PETP yarns common to all phases of the research. The main members consisting of 8 ply yarn coated with PVC are immersed and tested for their mechanical properties as well as the bare yarns, in the same conditions.

3. SUMMARY OF RESULTS OF THE TWO PREVIOUS PHASES

The main results of the first and second phase have already been published (Jailloux & al., 1992 ; Anderson & al., 1992).

3.1 *First phase*

The first phase showed that with a pH between 1 and 10, hydrolysis induces a loss of tensile strength that remains rather constant (below 0.8% per day at 95°C). Two mechanisms of degradation were found : the one that prevails at pH lower than 10 is usually referred to as "inner" hydrolysis and results in molecular cuts of the core material.

Above a pH of 10, caustic soda and saturated lime to a much greater extent produce the "outer" hydrolysis, which is a fast erosion of the fibre superimposed to the slower inner degradation. The rate found with saturated lime at pH 13 (i.e. in conditions alike those met inside fresh concrete or within lime or cement stabilized soil) goes beyond 20% per day at 95°C.

It was also demonstrated that salts with sodium or calcium cations (such as the ones found in sea water or deicing salts) have no significant influence on hydrolysis at a pH value less than 10.

3.2 *Second phase*

In this second phase of the research program, five different polyester yarns were exposed at 80°C in three media : water, hydrochloric acid HCl (pH 1), and caustic soda NaOH (pH 12). It revealed that after 300 days the degradation in water at 80°C induced a loss of strength of 45 to 60% for the high tenacity yarns. The low tenacity fibre exhibits a greater loss rate, around 85 to 95%.

The degradation rate in the case of the acid media (pH 1) is similar to what is observed in water, but the degradation starts immediately, whereas in water a delay is usually observed before the mechanical degradation begins. The resulting loss of strength after 300 days exposure is 10 to 15% greater than in water.

In the case of caustic soda (pH 12) less than 20% of the original strength of the high tenacity yarns is left after 300 days. It can be noted however that the yarns still look superficially undamaged .

The other investigations showed that :

- The residual strength decreases with the molecular weight, which presents a linear relationship with the CEG except in the case of degradation due to caustic soda. A simple equation can be derived :

$$\text{CEG count } (\mu g/g) = 1\,200\,000/Mn - 22$$

- The density is in linear relationship with the number of chain scissions per macromolecule (xt) ; for example the relation obtained for high tenacity yarns can be written as follows :

$$d\,(kg/m^3) = 1401 + 4.27xt$$

From this density measurement it is possible to calculate the crystalline fraction (taking into account the crystallised mass at a density of 1.46 and the amorphous mass at a density of 1.33). This approach clearly shows that in the hydrolysis process, the crystallisation rate increases.

- The degradation after a given time depends on the CEG count in the initial state. This is important for quality control for example : the greater the CEG is in the new state, the greater will be the hydrolytic degradation. The CEG count, which is easy to determine, seems to be a very interesting tool to control and follow the behaviour of PETP yarns, whereas the viscosity determination or the GPC technique might be too sophisticated in civil engineering.

4. EARLIEST RESULTS OF THE THIRD PHASE

4.1 *Effect of temperature*

Temperature is used as the accelerating factor because only high temperature testing gives significant results within a reasonably short time. The rate of hydrolysis depends on temperature, according to Arrhénius' law, whose principle is expressed by the equation : $A = A_0 * e^{-E/RT}$ where :

A is the parameter of the kinetics (for example the rate of loss of strength)

R is the gas constant (2 cal/mole*K)

T is the absolute temperature (K)

E is the activation energy, of about 25000 cal/mole in the particular case of polyester hydrolysis.

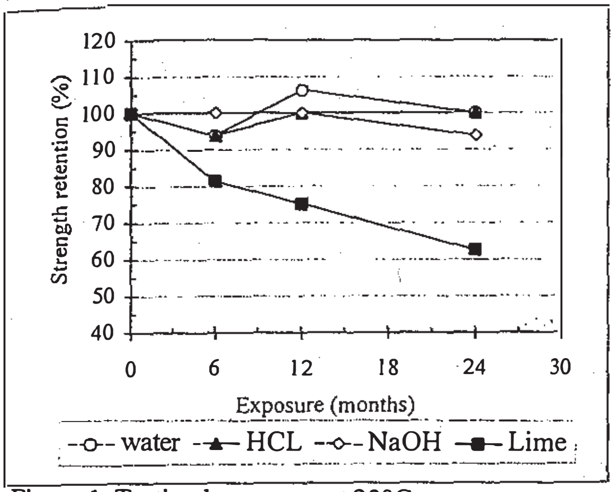

Figure 1. Testing bare yarns at 23°C.

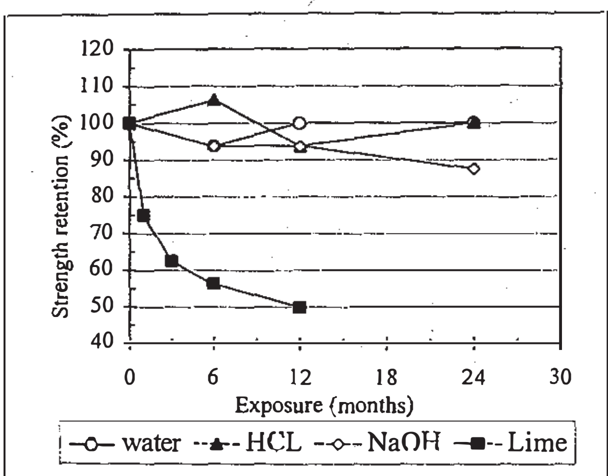

Figure 2. Testing bare yarns at 50°C.

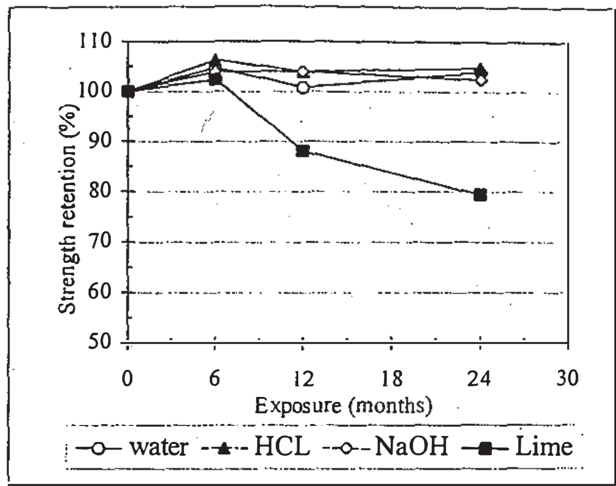

Figure 3. Testing PETP geogrid at 23°C.

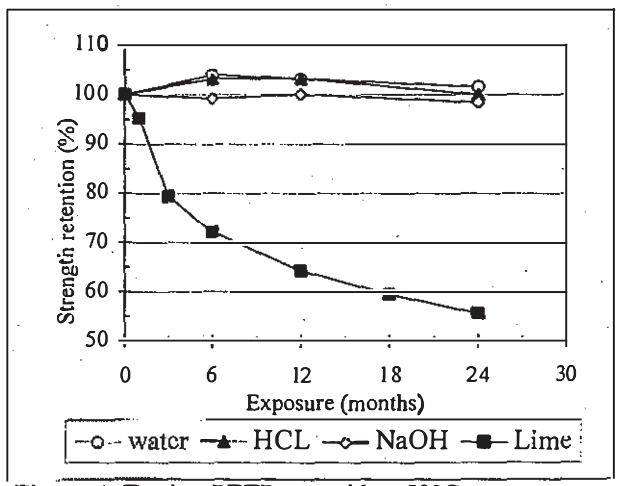

Figure 4. Testing PETP geogrid at 50°C

This value is calculated from test results obtained at temperatures above the glass transition temperature (Tg) which is around 65°C for PETP (above Tg polyester has a rubbery amorphous phase, below Tg the amorphous phase is glassy).

The Arrhénius' equation allows the computation of the degradation rate at any temperature, provided that the degradation mechanism does follow the same behaviour law. However, sound and precise long-term data is not yet available to confirm that the above value of activation energy is still valid for lower temperatures. This is the reason why TAI decided to launch a long-term experiment (which should last 15 years) at the ambient temperature of 23°C and also at 50°C, in order to get an intermediary point, below Tg.

The figures 1 to 4 present the results of the strength retention obtained during the first two years for the bare yarns as well as for the finished geogrid product.

As expected for these low temperatures and over this short period of time, the rate of hydrolysis does not induce noticeable losses in non-agressive media like water, nor in acidic or even alkaline media. Conversely, it can be noted that there is already a significant loss of strength in saturated lime and this offers one first opportunity of assessing the Arrhénius coefficient in this range of temperature. Surprisingly, the activation energy in such conditions lies around 15000 cal/mole rather than the 25000 or so indicated before. Two hypotheses may then be brought forward : either the mechanism of degradation that prevails with saturated lime differs from the one observed in more neutral conditions, or the activation energy of the degradation phenomena is significantly affected by the glass transition temperature.

Further results are expected to clarify this very important point and help have a better insight into the mechanism and kinetics of polyester hydrolysis. Should the second hypothesis prevail, it should be noted that extrapolating the high temperature results to ambient temperature with too high an activation energy would lead to a too low degradation rate.

4.2 *Effect of coating*

Comparing figures 1 and 3, and 2 and 4, shows that the thin PVC coating on the yarns provides a protection of about one year beyond which comparable level and rate of degradation are observed. This is inevitable since the coating cannot prevent the penetration of water. It is thus advisable not to take acoount of this protection, whose function is mainly to keep the yarns together and protect them from abrasion.

5. PRACTICAL CONSEQUENCES

It is certainly much too early to infer precise conclusions from the hypotheses and preliminary estimates presented in Section 4 , regarding actual applications and real environments. However a few practical and careful recommendations can be made, at this stage of knowledge.

5.1 *Reduction factor for design*

As far as hydrolysis in about neutral (or acidic) environments is concerned, figures 1 to 4 show that no significant loss could be measured after two years at 23° or even 50°C. However, the rate of degradation of a high tenacity fiber immersed in pure neutral water, as measured by TAI in the 2nd phase of the research program, was of the order of 0.17% per day at 80°C. Based on this value and on the two possible hypotheses regarding the activation energy which were considered above, we can see in table 1 below that the rate of degradation might lie between 3% and 30% or so after 70 years at the ambient temperature of 20°C.

Hypothesis		Activation Energy	70 yrs 20°C
E constant		E = 25000	3 %
Change in	t > 65°C	E = 25000	
E below t_g	t < 65°C	E = 15000	30 %

Table 1. Potential strength losses in pure water, at 20°C after 70 years.

This is nothing more than an indication, bearing in mind the imprecision which still marks these calculations and the fact that the presumption of two Arrhénius coefficients requires further validation. It nevertheless substantiates the recommendation that a "degradation reduction factor" of the order of 2/3 should still be considered at the design stage, for permanent structures and ordinary "non-aggressive" enviroriunents.

5.2 *Fresh concrete and lime treated backfill*

One thing is clearly confirmed at this stage : saturated lime at pH 13 is very detrimental to polyester fibres, even at ambient temperature. This means that polyester based geotextiles or soil reinforcements must not be used in combination with lime or cement stabilized soil ; they must not be either embedded into fresh concrete and no fresh concrete should be poured against polyester based geosynthetics.

5.3 *Direct contact with concrete*

Special attention must be paid to the case of polyester fibres in direct contact with set concrete, which might be the case for example at the facing of a retaining structure.

The relevant pH is of the order of 10.4. The results obtained at 95°C (1st phase) showed that the rate of degradation at a pH between 10 and 12 was 1.5 to 2.0 times larger than it was for pure water. Based on table 1, this leads to the potential strength losses shown in table 2, for the same hypotheses and again pending further validation.

Hypothesis		Activation Energy	70 yrs 20°C
E constant		E = 25000	6%
Change in	t > 65°C	E = 25000	
E below t_g	t < 65°C	E = 15000	60%

Table 2. Potential strength losses in contact with set concrete (pH 10.4) at 20°C after 70 years.

This does not take into account however the fact that the temperature is often higher than 20°C at the facing. It is therefore highly advisable that direct contact is avoided, and a protection is interposed, between polyester based geosynthetic reinforcements and any concrete structures or facing units.

6. CONCLUSIONS

The first two phases of the TAI research program have already produced data which will help better understand the mechanism of degradation and to quantify the effects of hydrolysis on polyester products.

The earliest results of the third phase after only two years confirm the aggressivity of saturated lime on high tenacity polyester at ambient temperature.

The activation energy which allows to extrapolate the results obtained at elevated temperature to lower temperatures seems to be affected by either the mechanism of degradation in alkaline media, or the glass transition temperature. This should be clarified after the next retrieving and analyses, which are scheduled after 5, 10 and 15 years of exposure (i.e. in years 2000, 2005 and 2010).

In the case of usual and about neutral environments the second hypothesis leads to the conclusion that the design reduction factors which were already recommended are appropriate. It also confirms the necessity of avoiding direct contact between polyester geosynthetics and concrete.

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