Acceleration of chemical degradation of polyester reinforcement products under mechanical stress in high alkaline conditions

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ABSTRACT: For a safe design of geosynthetic reinforced structures the long term behavior and especially the available resistant tensile force over the time under variable boundary conditions, such as temperature, chemical influences or loading conditions, has to be well known and understood. The known effects on the tensile strength, are considered in the design by applying so called reduction factors, e.g. for creep, installation damage or chemical degradation. Those reduction factors are determined separately without considering a possible interdependency. The main mechanism of the chemical degradation of polyester in high alkaline environment is the so called alkaline or "external" hydrolyses. In contrast to the internal hydrolyses, which provokes an evenly distributed, very slow degradation of the whole cross-section of the synthetic material, the external degradation generates a much faster "surface corrosion" with creation of fissures or cracks. If this does occur while the material is loaded, the fissures are widened and their propagation are dramatically accelerated. This results in much faster loss of strength. The paper reports on the consequence on the long term tensile strength if a PET reinforcement in high alkaline environment is subjected to tensile load.

Keywords: polyester, high pH-value, accelerated degradation, loos of strength

1 INTRODUCTION

In general engineering design praxis the knowledge of material characteristics, especially those responsible for the stability of a structure, is fundamental. It is evident that this does include also the understanding of the effect of degradation mechanisms on the material properties with the corresponding boundary conditions of the structure (external influences). A safe prediction of the e.g. strength evolution over time under consideration of e.g. temperature, mechanical loading or chemical exposure is therefore required. This does presume that the degradation mechanisms for different raw materials and the interdependency, if any, of different degradation mechanisms are known.

Geosynthetic reinforcement products are prone to different degradation mechanisms which result from creep (elongation under constant loading), chemical exposure or cyclic loading condition. The short term tensile strength is therefore reduced by different reduction factors to account for the reduced long term tensile strength. The tensile force is not only reduced due the degradation mechanisms but also due to the effect of installation damage, which considered via a further reduction factor.

Those reduction factors are determined independent from each other, which does indirectly include the assumption, that there is no interdependency between the different degradation mechanisms. In fact, it is quite difficult to detect the interdependencies if multiple factors are involved and especially, when only certain combinations result in a change of the degradation behavior of certain mechanical properties.

This paper deals with such a behavior, which does occur if geosynthetics made from polyethylene terephthalate (PET) are under tension in damp environments with pH-values greater the 9.

2 MECHANICAL PROPERTIES OF PET IN HIGH ALKALINE ENVIRONMENTS

2.1 *General degradation mechanism*

The mechanism of the chemical degradation of PET in a high alkaline environment (pH-value > 9) is marked by alkaline, or so-called external hydrolysis, which is always accompanied by an internal hydrolysis in damp earth.

The internal hydrolysis also occurs in soil with a neutral pH-value (4 ≤ pH ≤ 9) and results in a mechanical degradation which takes place evenly over the entire cross-section. The degradation process itself is relative slow and the loss of strength for a time frame of 120 years quite small.

The external hydrolysis causes a "surface corrosion", which results in cavities and cracks. Furthermore the speed of degradation process is much higher as well as the loss of strength. Figure 1 shows a PET geogrid strand damaged by external hydrolysis to the point of perforation. It has been stored, stress-free (without any tensile load) in a saturated Ca(OH)2 solution (limewater).

The damage pattern between the internal and external hydrolysis does differ significantly. According to the current practice the reduction in tensile strength over time in relation to the pH-values is considered by applying the corresponding reduction factor when determining the long term tensile strength of the product.

2.2 *Degradation mechanism under tensile loading*

If PET products are placed in high alkaline environments and at the same time subjected to tensile forces the degradation process concerning the loss of tensile force does speed up significantly. This is due to the fact, that the tensile forces expand the micro cracks and the cracks propagate, which does result in reduced cross section area and therefore in reduced tensile strength. Evidence of this rheological phenomenon is provided in published investigations (Müller 2013, Müller-Rochholz and Bronstein 1994). Figure 2 to Figure 4 illustrating the above described mechanism.

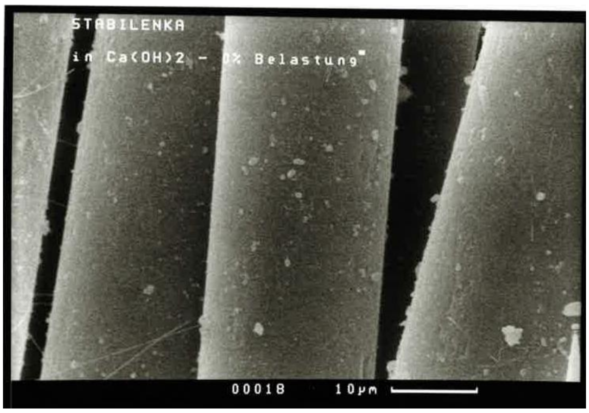

Figure 1: PET fibres after being stored for 91 days in Ca(OH)2 without stress at 40°C (Müller-Rochholz and Bronstein 1994)

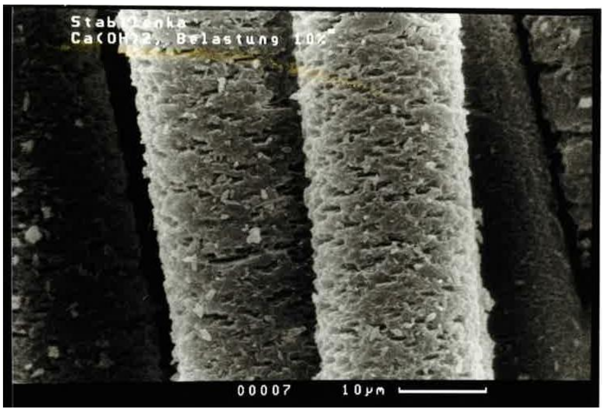

Figure 2: PET fibres after being stored for 55 days in Ca(OH)2, stressed with 10% of the maximum tensile strength at 40 °C (Müller-Rochholz and Bronstein 1994)

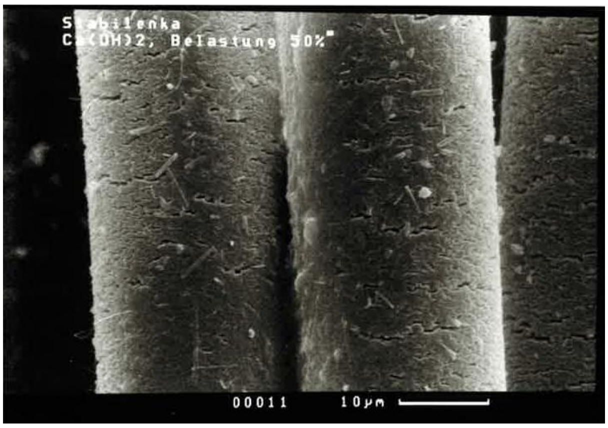

Figure 3: PET fibres after being stored for 14 days in Ca(OH)2, stressed with 50% of the maximum tensile strength at 40℃ (Müller-Rochholz and Bronstein 1994)

The images in Figure 1 to Figure 3 are pictures taken with a scanning electron microscope (SEM) of the surfaces of PET fibers, which were simultaneously exposed to an alkaline environment (limewater, pH = 12.6 measured at 20℃) at 40℃ and mechanical stress, for a short period of time (Müller-Rochholz and Bronstein 1994).

The damage patterns show the effect of mechanical tensile stress on the formation of notches and cracks during external hydrolysis. As a result of these investigations, it was possible to detect a causal relationship between the surface structure of the PET fibers under examination during external hydrolysis, and the applied stress. The far greater damage to the surface in (Figure 2), compared to the stress-free storage after 91 days in (Figure 1), has already occurred after 55 days at a relatively low mechanical tensile stress of 10% of the maximum tensile strength (% of max. tensile strength) of the material in an alkaline environment.

The stress-dependent strength development of the PET fiber examined in (Müller-Rochholz and Bronstein 1994), is summarized in Table 1.

Table 1. Effect of tensile stress on the residual strength of PET reinforcement in Ca(OH)2 at 40℃ after a storage period of 21 days

Mechanical stress as % of max. tensile strength	Residual tensile strength in %	Reduction factor A_4
0	93.5	1.07
10	88.4	1.13
25	64.6	1.55
50	0*	-
75	0*	-

(* samples ruptured during testing)

The numbers in Table 1 demonstrate very clear the influence of the stress state of the polymer material on the reduction factor A_4 for the chemical environmental influences on the PET reinforcement in a high alkaline environment.

The notches caused by progressive outer hydrolysis alters the distribution of stress in the material's cross section. Under the effects of tensile force, peak stresses are induced clearly in the notch valleys, altering significantly the mechanical behavior and hence affecting the creep fracture and creep properties. This statement can be examined with the residual strength compiled in Table 1. The investigations took a load equaling 50 % of the freshly manufactured material's ultimate tensile strength to correspond to a 53.5 % utilization coefficient based on the residual strength of the unloaded product embedded for 21 days in lime milk (50 %/ 93.5 %). Under the assumption that the creep behavior does not deteriorate under chemical ageing, the expected service life of the analyzed fibers would equal several hundred years when, even at 40° C, the utilization coefficient corresponds to 53.5 % of the ultimate tensile strength based on the characteristic creep fracture properties determined separately. During the MÜLLER-ROCHHOLZ & BRONSTEIN tests, however, the material failed to withstand the loading for even three weeks. The assumption, therefore, of interdependency between outer hydrolysis and simultaneous mechanical loading appears a plausible explanation of the large discrepancy in the creep fracture times, yet the use of reinforcement without mechanical loading would be a contradiction in terms. Thus, for example, a stress of 25% of the max. tensile strength after 21 days at 40°C causes an additional reduction in the residual tensile strength by the factor of 1.55/1.07=1.45, compared to the stress-free degradation of the reinforcement element in this environment over the same period of time.

In other words, an isolated determination of the reduction factors A_1 for the creep rupture behavior and A_4 for the chemical effects of an alkaline environment does not provide any reliable values for the static considerations of composite structures of geosynthetic reinforcement and soil because their interdependency are not taken into account.

Due to those combined effects PET reinforcement elements should not be used in high alkaline environments in long term applications. For those applications suitable raw material for the reinforcement should be selected, such as e.g. polyvinyl alcohol (PVA).

3 CONCLUSION

The external hydrolysis of PET reinforcement products in a highly alkaline environment leads to a reduction in the cross-section area and thus to the degradation of the mechanical strength of the geosynthetic elements, primarily through surface corrosion and the formation of notches on the surface. If tensile forces are acting, local weaknesses will be extended and the rate of crack propagation increases. It is therefore concluded that it is imperative for the reduction factors for PET reinforcement products in a high alkaline environment to be determined from reinforcement elements that are under tensile stress. Stating a reduction factor for chemical influences for PET reinforcement in an alkaline environment that has been determined from test specimens that are stored stress-free, does not reflect the actual failure mechanism and produces misleading results when the long-term strength is determined. Above all, this will not meet the safety requirements for geotechnical structures.

REFERENCES

Müller, W. (2013). Alterung von Bewehrungsgittern aus Polyester. Geotechnik, S. 359-366.

Müller-Rochholz, J., & Bronstein, Z. (1994). Einfluß von Zugbeanspruchung auf das Hydrolyseverhalten von Polyester (PET).